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Factors controlling the concentrations of thirteen rare metals in sea-water*

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ABSTRACT

The following factors controlling the concentrations of thirteen metals (Zn, Cu, Pb, Bi, Cd, Ni, Co, Hg, Ag, Cr, Mo, W, V) in sea-water were studied: (1) precipitation of insoluble compounds with ions normally present in aerated sea-water, (2) precipitation of sulphides locally in reducing environments, (3) adsorption by ferrous sulphide, hydrated ferric oxide, hydrated manganese dioxide, apatite, clay, and organic matter. The precipitation reactions were investigated first by calculations based on solubility data, and then by experiments in which equilibrium concentrations of the metal ions were determined in sea-water in contact with their precipitates. Adsorption was measured by adding or precipitating the various adsorbents in sea-water samples containing an excess of one of the metal ions.

The principal conclusions are: (1) Sea-water is greatly undersaturated with respect to all thirteen metals; in other words, precipitation of compounds with the ions normally present in aerated sea-water, even under extreme conditions of temperature and pH, cannot be responsible for the observed concentrations. (2) Local precipitation of sulphides is a possible control mechanism for seven of the elements (Cu, Zn, Hg, Ag, Cd, Bi, Pb), but is probably not the chief control, because the concentrations are unrelated to sulphide solubilities. (3) Adsorption is a possible mechanism for all elements except V, W,

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Ni, Co, and Cr; if Cr is assumed to be removed by local reduction and precipitation of the hydroxide, and the other four metals by organic reactions, the existing concentrations can be fairly adequately accounted for. Adsorption processes supplemented by organic reactions also furnish a qualitative explanation for the distribution of rare metals in sedimentary rocks of marine origin. These conclusions can probably be extended to other metals in the middle of the periodic system, but not to those on either side.

INTRODUCTION

RARE metals are notably concentrated in certain marine sedimentary rocks, especially black shales and phosphorites. The source of the metals is commonly thought to be the sea-water in which the sediments were deposited. This postulate leads to several questions regarding the rare-metal content of sea-water. In what form do the various metals exist in the sea? By what process or processes may the metals be removed from sea-water during sedimentation? What factors control the amount of a given metal in sea-water? Why, for instance, should the concentration of copper lie between 1 and 10 parts per million rather than between 0.1 and 1, or between 10 and 100? Such questions are the subject matter of this paper.

The investigation has been limited to simple experiments and calculations of a strictly exploratory nature. Since the problem concerns a complex natural system in which many variables are necessarily uncontrolled, the effort required to obtain more precise results is hardly justified. The discussion is furthermore restricted to present-day sea-water, and does not touch the question as to how the rare-metal content of the sea may have changed in the geologic past.

The fact that sea-water is apparently undersaturated with respect to several of the rare metals has been noted repeatedly. GOLDSCHMIDT (1937) suggested that rare-metal concentrations are kept low by adsorption, particularly on iron-oxide precipitates. HARVEY (1945, p. 33) reports experiments showing that copper salts are readily soluble in sea-water, but that excess copper can be markedly reduced by adsorption on clay or organic matter. The importance of adsorption is also emphasized by GOLDBERG (1954), who points out that nickel chloride dissolves in sea-water but that Ni^{++} is readily adsorbed by manganese dioxide. GOLDBERG further suggests that the distribution of rare metals in iron oxide and manganese oxide precipitated from sea-water should indicate which metals are present in the sea as cations and which as anions, since colloidal particles of the two oxides carry opposite electric charges.

A conceivable explanation for the observed concentrations of rare metals in the sea is that the present amounts represent simply the accumulation to date of material weathered from the land and carried to the sea during geologic time. This possibility was disposed of many years ago by GOLDSCHMIDT (1932), and his method of calculation has been verified by CORRENS (1948). GOLDSCHMIDT estimated for each element the total quantity weathered and eroded from the land; a comparison of these figures with concentrations of metal ions in sea-water shows that for all metals except possibly sodium the amount added to the sea far exceeds the present quantity.

A part of GOLDSCHMIDT's table, showing the effectiveness of removal of rare metals from the sea, is reproduced as Table 1. (The table is a revision of the original, taken for the most part from RANKAMA and SAHAMA, 1950, p. 295.)

Most of the figures in the table are somewhat uncertain. The extent of the uncertainty for the analytical values in the third column is well illustrated by the surprisingly high concentrations of Mo, Ni, V, and Cr (numbers in parentheses) recently reported by BLACK and MITCHELL (1952). GOLDSCHMIDT's estimates of amounts supplied to the sea (second column) are of course even less reliable, since they depend not only on limited analytical data but also on at least two somewhat questionable assumptions: that the sodium of sea-water has been increasing through geologic time to the present, and that rare metals go into solution during weathering in proportion to their concentrations in igneous rocks.

Table 1. *Effectiveness of removal of rare metals from the sea*

<i>Metal</i>	<i>Calculated amount supplied to the sea during geologic time (p.p.m.)</i>	<i>Concentration in sea-water at present (p.p.m.)</i>	<i>Percentage remaining in solution (per cent)</i>
Ag	0.06	0.00015-0.0003	0.25-0.5
Bi	0.12	0.0002	0.2
Mo	0.6-9	0.0003-0.0007 (0.012-0.016)	0.003-0.12 (0.1-2.7)
Cd	0.09	0.000032-0.000075	0.04-0.08
Pb	9.6	0.003-0.008	0.03-0.08
Hg	0.046-0.3	0.00003	0.01-0.07
Cu	42	0.001-0.015	0.002-0.04
Zn	79	0.005-0.021	0.006-0.03
W	0.9-41	0.00009-0.0001	0.0002-0.01
Co	14	0.0001	0.0007
Ni	48	0.0001-0.0005 (0.0015-0.006)	0.0002-0.001 (0.003-0.012)
V	90	0.0003 (0.0024-0.007)	0.0003 (0.003-0.008)
Cr	120	0.00004-0.00007 (0.001-0.0025)	0.00003-0.00006 (0.0008-0.002)

Data chiefly from MASON (1952) and RANKAMA and SAHAMA (1950).

Data for Mo partly from KURODA and SANDELL (1954); for Cd from MULLIN and RILEY (1954); for W and Cr from ISHIBASHI (1953).

Numbers in parentheses for Mo, Ni, V, and Cr are spectrographic determinations by BLACK and MITCHELL (1952); for these same four elements ISHIBASHI (1953) gives values between those of MASON and those of BLACK and MITCHELL.

Nevertheless, even large revisions in some of the values could hardly change the general conclusion that the metal content of the present ocean is but a tiny fraction of the amount of metal ions poured into it. It is reasonable to suppose further that each metal long ago reached a concentration determined by a balance between the processes adding it to sea-water and processes removing it from sea-water.

Another inference from Table 1 is that the processes of removal are more effective

for some metals than for others. A few metals, for example Ag and Bi, are present in a relatively large fraction (greater than 0.2 per cent) of the amount supplied; a second group, including Cu, Zn, and Pb, have their concentrations reduced to 0.005–0.2 per cent of the amount supplied; and a third group, including V and Ni, show still more effective removal. The possible significance of these differences is considered below.

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INFERENCES FROM PHYSICO-CHEMICAL DATA

General statement.—The concentrations of some metals in sea-water are controlled by the slight solubilities of their compounds with the ions ordinarily present in the sea. The amount of Ca^{++} , for example, depends chiefly on the solubility of CaCO_3 . The possibility that rare-metal concentrations are similarly controlled is examined first by calculations based on solubility data, and then by experiments designed to check and supplement the calculations.

The abundant anions of ordinary oxygenated sea-water are Cl^- , SO_4^{--} , and CO_3^{--} . These are known to form relatively insoluble compounds with many of the rare metals, and solubility products permit calculation of the amounts of the metals that can exist in equilibrium with them in the sea. Rare metals that exist as anions in sea-water might be precipitated by one or more of the abundant cations (Na^+ , K^+ , Mg^{++} , Ca^{++}), but solubility data are insufficient to explore this possibility in detail. The less abundant anions of the sea might also play a role if solubilities of their compounds with the rare metals are extremely low; this possibility is examined below, but for the present only the abundant ions are considered.

In order to carry out the calculations, one must know first the form in which the rare metals exist in sea-water, and secondly the effect of other ions in the sea on solubility products. Those questions are examined in the following sections.

Mode of occurrence of rare metals in aerated sea-water.—Metals can exist in the sea in at least four different forms: (1) as a part of living organisms, (2) as colloidal particles, (3) adsorbed on other colloidal particles, and (4) in true solution. The first three may be difficult to distinguish experimentally one from the other, but all represent metals in the form of suspended particles as opposed to true solution. That gold may exist largely in particulate form is indicated by HABER's (1928) work; more recent studies by PATTERSON *et al.* (1953) suggest that lead occurs at least partly as suspended particles. It is probable that particles account for a part

of the concentration of other metals also, so that calculation from physico-chemical data can give at best only a minimum figure for the amount of a metal which should be present at equilibrium with the ions of sea-water.

The nature of the ions (or neutral molecules) that exist in true solution can be specified with confidence for some of the metals but only guessed at for others. Copper, for example, in chloride solution forms the ions Cu^{++} , CuCl^+ , CuCl_3^- , and CuCl_4^{--} , as well as undissociated CuCl_2 . According to the data of BJERRUM (1950), a solution with 0.55M Cl^- (like sea-water) should have mostly Cu^{++} , about one-third as much CuCl^+ , one-thirtieth as much CuCl_2 , and negligible quantities of the negative ions. The numerical values of the equilibrium constants may not be quite the same in sea-water as in BJERRUM's solutions, and there may be some complication from the formation of $\text{Cu}(\text{OH})^+$, but it seems certain that dissolved copper will be largely in the form of positive ions, and it seems at least probable that the most abundant ions will be Cu^{++} and CuCl^+ . Similarly, zinc is present in sea-water chiefly as Zn^{++} and ZnCl^+ (from the data of SILLÉN and LILJEQVIST, 1944), cadmium as CdCl^+ and CdCl_2 (from the data of VANDERZEE and DAWSON, 1953), and lead chiefly as PbCl^+ (GUCKER and GARRELS, 1949). Mercury and silver, on the other hand, exist chiefly as negative ions, HgCl_4^{--} and AgCl_2^- (LINDGREN, JOHNSON, and SILLÉN, 1947; JONTE and MARTIN, 1952). For cobalt, more indirect reasoning from adsorption studies leads KURBATOV, WOOD, and KURBATOV (1951) to the conclusion that the "effective valence" of cobalt in chloride solutions is 1.2, which means that the principal ions present are probably Co^{++} , CoCl^+ , and perhaps $\text{Co}(\text{OH})^+$ also. No data are available for nickel, but its behaviour is probably similar to that of cobalt. The available information about bismuth, as summarized by LATIMER (1952, p. 122) and by BABKO and GOLUB (1953), indicates that BiO^+ is predominant over BiCl_4^- and that Bi^{+3} is very minor. Chromium in aerated sea-water would exist as CrO_4^{--} ; molybdenum and tungsten are doubtless also present in anions, but the formulas are unknown. Vanadium, according to the data of DUCRET (1951), should be present almost entirely in the quinquevalent form, chiefly as H_2VO_4^- , but perhaps in part as $\text{H}_3\text{V}_2\text{O}_7^-$. The ions and molecules discussed in this paragraph are listed in the first column of Table 2.

Effect of sea-water on solubility products.—Solubility products given in the literature are measured in dilute solutions or extrapolated to infinite dilution, hence are not directly applicable to so complex and concentrated a solution as sea-water. The effect of electrolytes on a solubility product can be calculated by the formulas of the Debye-Hückel theory, but only up to an ionic strength of about 0.1. (The ionic strength of a solution is a measure of its total concentration; it is defined as half the sum of the concentrations of the ions present, each concentration being multiplied by the square of the valence of the ion.) For sea-water, with an ionic strength about 0.7, direct calculation is impossible. A rough idea of the factor by which solubility products must be modified can nevertheless be obtained by inspection of tables of activity coefficients for various salts (LATIMER, 1952, p. 354). For uni-univalent salts, activity coefficients in solutions of ionic strength 0.7 cluster around 0.7; for di-divalent salts, around 0.12; and for uni-divalent and di-univalent salts, around 0.4. There are notable exceptions, but the values are sufficiently uniform to justify their use as tentative approximations.

Table 2. Calculated concentrations of metal ions in saturated solutions

Chief metal ion or ions	Insoluble compound	Solubility product	Factor	Calculated concentration of metal in saturated solution (p.p.m.)
Zn ⁺⁺ , ZnCl ⁺	ZnCO ₃	2×10^{-10}	70	4.6
Cu ⁺⁺ , CuCl ⁺ , Cu(OH) ⁺ ?	CuCO ₃	2.5×10^{-10}	70	5.7
PbCl ⁺ , Pb ⁺⁺	PbCO ₃	1.5×10^{-13}	70	0.01
BiO ⁺ , BiOCl?, BiCl ₄ ⁻ ?	BiOCl	7×10^{-9}	2	0.006
CdCl ⁺ , CdCl ₂ , Cd(OH) ⁺ ?	Cd(OH)Cl	3.2×10^{-11}	16	105
Ni ⁺⁺ ?, NiCl ⁺ ?, Ni(OH) ⁺ ?	Ni(OH) ₂	1.6×10^{-16}	16	150
Co ⁺⁺ , CoCl ⁺ ?, Co(OH) ⁺ ?	(CoCO ₃ Co(OH) ₃)	8×10^{-13}	70	{0.02 0.01-0.08*
HgCl ₄ ⁻⁻	HgO			high
AgCl ₂ ⁻	AgCl			0.5-6
CrO ₄ ⁻⁻	CaCrO ₄ ?	7.1×10^{-4}	70	high
H ₂ VO ₄ ⁻ , H ₃ V ₂ O ₇ ⁻	V ₂ O ₅ · nH ₂ O	5×10^{-4}	2	high
Mg ⁺⁺	MgCO ₃ · H ₂ O	1×10^{-5}	70	84,000
Ca ⁺⁺	CaCO ₃	5×10^{-9}	70	70
Sr ⁺⁺	SrCO ₃	$3-16 \times 10^{-10}$	70	9-44
Ba ⁺⁺	BaSO ₄	1×10^{-10}	70	0.03

In the first column, ? following a formula indicates that the ion is probably present, but quantitative data are lacking. An ion underlined is the most abundant species present.

Concentrations in the last column are calculated for sea-water with Cl⁻ = 0.55*M*, OH⁻ = 10⁻⁶*M*, CO₃⁻⁻ = 0.0002*M*, SO₄⁻⁻ = 0.028*M*, temperature 25°C, and pressure 1 atm.

Data on Ca, Sr, Ba, and Mg included for comparison purposes only.

Solubility product for Cd from FEITKNECHT and REINMANN (1951), for V from DUCRET (1951), for Sr from WATTENBERG and TIMMERMAN (1937); all others from LATIMER (1952).

*Concentration of Co is 0.01 p.p.m. for *p*O₂ = 0.2 atm and 0.08 p.p.m. for *p*O₂ = 10⁻⁴ atm.

The solubility products as given for dilute solutions should accordingly be multiplied by the following factors:

for 1-1 salts, by 1 divided by (0.7)², or 2

for 2-2 salts, by 1 divided by (0.12)², or 70

for 2-1 salts, by 1 divided by (0.4)³, or 16

Results.—The results of using these factors are shown in Table 2. The first column lists the metals for which pertinent solubility data are available, and shows the form in which each metal most probably exists in sea-water. The second column shows for each metal the compound with a major ion of sea-water which, according to existing data, gives the lowest concentration of the metal in solution. Solubility products for these compounds are listed in the third column; all are from LATIMER except the ones for cadmium (from FEITKNECHT and REINMANN, 1951) and vanadium (from DUCRET, 1951), and one of the two for strontium (from WATTENBERG and TIMMERMAN, 1937). The fourth column shows the factors

used to multiply the solubility products to correct for the ionic strength of sea-water. The fifth column gives the calculated equilibrium concentrations for sea-water at 25°C containing 10^{-6}M OH^- , 0.55M Cl^- , 0.0002M CO_3^{--} , and 0.028M SO_4^{--} .

The metals Ag, Hg, and Co require more complicated calculations than do the others. Ag exists chiefly as the complex ion AgCl_2^- , for which slightly different dissociation constants are given by JONTE and MARTIN (1952), SHCHIGOL (1952), and BERNE and LEDEN (1953); figures for AgCl_2^- , calculated from the two extreme values, are given in Table 2. Hg also exists chiefly as a chloride complex, and the amount of this complex that can form is limited by the solubility of HgO ; the calculation thus involves the dissociation constant of the complex and the solubility product of HgO , both given by LATIMER (1952). The amount of Co^{++} is limited either by the oxidation potential of its reaction with oxygen and the solubility of Co(OH)_3 , or by the solubility of CoCO_3 ; the two processes give the same equilibrium concentration. No attempt was made to correct for ionic strength in the calculations for these metals.

The limitations of these calculations should be emphasized. The correction for ionic strength is extremely rough; the compounds for which solubility products are recorded may not be the ones actually formed in sea-water (copper, for instance, forms a basic carbonate rather than the simple carbonate); and solubilities of some metals may be affected by the formation of complexions.

Discussion.—The general lack of agreement between calculated concentrations and actual concentrations in sea-water is shown by Table 3, where the calculated values are repeated in the second column and concentrations in the sea are given in the fourth column (figures in the third and fifth columns are discussed in the next section). The last three metals in the table (Ca, Sr, Ba) show about as much agreement as could be expected, in view of the assumptions involved, and the agreement suggests that these metals may indeed have concentrations controlled largely by solubilities. The calculated figure for Mg has little meaning, since this metal would most likely be controlled by the solubility of dolomite rather than the simple carbonate; a figure for the solubility product of dolomite has been given by HALLA (1935), but the correction for ionic strength is so uncertain that calculation seems pointless. For all other metals in the table the calculated figures exceed the observed amounts, and for all except Pb and Bi the discrepancy exceeds a factor of 100. This could mean that the assumptions underlying the calculations are grossly inaccurate; but the fact that the discrepancies are all in one direction, together with the fact that the assumptions appear to be justified for Ca, Sr, and Ba, suggests the alternative interpretation that amounts of these rare metals in the sea are not controlled by the solubilities of the compounds listed in Table 2.

Another possibility for the control of concentrations would be the solubility of compounds of the rare metals with some of the less abundant ions of sea-water. Nickel, for example, is obviously not dependent on the solubility of NiCl_2 , NiSO_4 , NiCO_3 , or Ni(OH)_2 , but conceivably it might form a very insoluble compound with F^- , Br^- , I^- , BO_2^- , PO_4^{-3} , AsO_4^{-3} , or SeO_4^{--} . A study of this possibility requires calculating the amount of Ni^{++} that could exist in sea-water with the

Table 3. Comparison of calculated and measured concentrations of metals in saturated solutions with observed concentrations in sea-water

Metal	Concentration in saturated solution (p.p.m.)		Concentration in sea-water (p.p.m.)	Ratio of measured concentration to concentration in sea-water
	Calculated	Measured		
Zn	4.6	1.2-2.5	0.005-0.021	60-500
Cu	5.7	0.4-0.8	0.001-0.015	30-800
Pb	0.01	0.3-0.7	0.003-0.008	25-200
Bi	0.006	0.04	0.0002	200
Cd	105	4-1000	$32-75 \times 10^{-6}$	10^5-10^7
Ni	150	20-450	0.0001-0.0005 (0.0015-0.006)	$4 \times 10^4-5 \times 10^6$ ($3 \times 10^3-3 \times 10^5$)
Co	0.01-0.08	25-200	0.0001	$2.5 \times 10^5-20 \times 10^5$
Hg	high	100-1000	0.00003	$3 \times 10^6-30 \times 10^6$
Ag	0.5-6	2.0-2.5	0.00015-0.0003	$0.7 \times 10^4-1.7 \times 10^4$
Cr	high	high	$4-7 \times 10^{-5}$ (0.001-0.0025)	$>10^6$ ($>10^4$)
Mo		25-750	0.0003-0.0007 (0.012-0.016)	$3.5 \times 10^4-2.5 \times 10^6$ ($1.6 \times 10^3-62 \times 10^3$)
W		2-200	0.0001	$2 \times 10^4-2 \times 10^6$
V ^{IV}	high	4-150	0.0003	$>10^4$
V ^V	high	>400	(0.0024-0.007)	$\left\{ \begin{array}{l} >10^3 \\ >10^6 \end{array} \right.$
Mg	84,000	36,000	1272	28
Ca	70	100-480	400	0.25-1.2
Sr	9-44	22	13	2.2
Ba	0.03	0.11	0.05	2.2

Parentheses indicate data from BLACK and MITCHELL (1952).

Data on Sr, Ba, Ca, and Mg from WATTENBERG and TIMMERMANN (1937).

known amount of each of these anions. To give all the calculations for each metal would be tedious, but the method may be illustrated with PbCO_3 and $\text{Pb}_3(\text{PO}_4)_2$. The concentration of Pb^{++} in equilibrium with the CO_3^{--} of sea-water (0.0002M) is given by

$$\text{Pb}^{++} = \frac{\text{solubility prod. of } \text{PbCO}_3}{\text{CO}_3^{--}} = \frac{1.5 \times 10^{-13}}{2 \times 10^{-4}} = 0.8 \times 10^{-9} \text{ mole/l.}$$

The concentration of Pb^{++} in equilibrium with PO_4^{-3} (using the maximum value for total phosphate given by SVERDRUP *et al.* (1946), 0.0035M, and using 8.5×10^{-12} as the dissociation constant of HPO_4^{--}) is given by

$$\text{Pb}^{++} = \sqrt[3]{\frac{\text{solubility prod. } \text{Pb}_3(\text{PO}_4)_2}{(\text{PO}_4^{-3})^2}} = \sqrt[3]{\frac{1.5 \times 10^{-32}}{(3 \times 10^{-6})^2}} = 1.2 \times 10^{-7} \text{ mole/l.}$$

Thus more lead could exist in the presence of the PO_4^{-3} in sea-water than in the presence of the CO_3^{--} , despite the greater insolubility of the phosphate. Similar

calculations have been carried out for all compounds of the other metals for which solubility data are known, and the result in each case is the same: equilibrium concentrations of metal ions permitted by the less abundant ions of sea-water are larger than the concentrations permitted by the major ions. This statement refers only to ions normally present in aerated sea-water, but not to ions which may exist locally in reducing environments, such as S^{--} ; the possible influence of such ions is considered below. The statement is also subject to limitations imposed by the scarcity of accurate solubility data. Nevertheless, a tentative generalization seems justified that, *according to calculation, normal aerated sea-water is undersaturated with respect to rare metals, except possibly for Sr and Ba.*

EXPERIMENTS WITH NORMAL, AERATED SEA-WATER

Experiment offers another approach to the problem of how effectively concentrations may be controlled by equilibrium with slightly soluble compounds. Rigidly controlled experiments in a medium as complex as sea-water would be prohibitively time consuming, but much suggestive information can be obtained from rapid semiquantitative work. The procedure adopted was to add a solution of each metal ion to a sample of sea-water until a precipitate formed, and then allow the mixture to stand until the metal ion concentration became constant, making the necessary adjustments throughout to keep the pH of the solution constant. This procedure should give, in favourable cases, an equilibrium value for the metal ion concentration in contact with the precipitate, and in any case it should give a maximum value. The equilibrium was then approached from the opposite direction by filtering off some of the precipitate and adding it to a new sample of sea-water, again adjusting the pH and measuring the metal ion concentration at intervals until it became constant. This should give a minimum value for the equilibrium concentration, and in cases where the two values did not coincide the equilibrium figure was assumed to lie between. Great accuracy was not attempted, and the nature of the various precipitates was not investigated. Whatever the precipitates are, they must be the ones formed in places where metal ions enter the sea in quantity (disregarding the possibility of very slow reactions); if such compounds play any role in holding metal concentrations at particular values, the experimental figures should have at least the same order of magnitude as the concentrations found in nature.

To analyze the sea-water samples, SANDELL'S (1950) colorimetric procedures were used. Colours were evaluated by visual comparison with standards. The validity of the analytical method was checked in each case by a series of tests on solutions of known metal concentration but otherwise identical with the solutions to be analysed. Slight modifications were necessary in some of the procedures, but less difficulty was found than anticipated in applying SANDELL'S methods to sea-water. Sufficient duplicate runs were made to insure reproducibility within at least a factor of 2. Examples of the kind of data obtained are given in Table 4.

Many of the experiments were tried both in artificial sea-water prepared by the Lyman-Fleming formula (SVERDRUP *et al.*, 1946, p. 186) and in natural sea-water. The natural sea-water was obtained through the courtesy of Professor

Table 4. Averages of solubility measurements

	1-20 hr	1-3 days	4-8 days	10-17 days	21-28 days	37-63 days
<i>Zinc</i>						
ZnCl ₂		1.3	5(?)		2.5	2.5
Zn ppt		1.2	1.7		1.2	
<i>Copper</i>						
CuSO ₄		0.59	0.76		0.75	
Cu ppt		0.87	0.61		0.65	
<i>Lead</i>						
Pb(NO ₃) ₂		0.33	0.29			
Pb ppt		0.4	0.67	0.71		0.53
<i>Bismuth</i>						
Bi(NO ₃) ₃	1.3	0.05	0.05			
Bi ppt	<0.02		0.03			
<i>Cadmium</i>						
CdCl ₂		400			3000(?)	1000
Cd ppt		0.5			2.5	4
<i>Nickel</i>						
NiCl ₂			405		455	
Ni ppt			35		23	
<i>Cobalt</i>						
CoCl ₂			153	218	196	
Co ppt			33		26	28
<i>Mercury</i>						
HgSO ₄			118			
Hg ppt	500				700	
HgO				1000		
<i>Silver</i>						
AgNO ₃	2.0	2.2				
Ag ppt			2.5			
<i>Chromium</i>	No ppt even after massive additions of K ₂ CrO ₄					
<i>Molybdenum</i>						
(NH ₄) ₂ MoO ₄	1950	1000	750			
Mo ppt		32		25		
MoO ₃	1800	1200		1000		
<i>Tungsten</i>						
Na ₂ WO ₄		400		280		
W ppt		<1		2		
WO ₃		43		160		
<i>Vanadium</i>						
V ⁺⁴ ppt				4.3	3.9	

Under each metal the first row of figures shows (in parts per million) the concentration of metal remaining in solution after the compound indicated has been added to sea-water until a precipitate forms. The second row shows the concentration of metal in solution obtained by adding some of the precipitate to a fresh sample of sea-water. Times of standing were different in different runs, hence are given as ranges rather than specific numbers of days. Most of the numbers are averages from several runs. In all experiments pH = 7.8-8.2 and temperature = 18°-23°C.

If VOSO₄ is added slowly to sea-water, a precipitate forms when about 16 p.p.m. of V is present, but the precipitate appears to dissolve on standing over a period of hours. A permanent precipitate forms only after enough has been added to give more than 150 p.p.m. of V in solution. Quinquevalent vanadium gives no precipitate, even after massive additions.

BJØRN FØYN, director of the Marine Biological Station of the University of Oslo, from the Oslo Fjord at Drøbak, about 40 km south of Oslo and 60 km north of the mouth of the fjord. It was obtained from a depth of 26 m by pumping through lead pipes, so of course could not be used in the experiments on this metal. The water had a salinity of about 30 parts per thousand, a little less than that in water from the open sea. Determinations of copper and zinc (after extraction from 200 ml with dithizone) in the water gave 0.0025 p.p.m. and 0.008 p.p.m. respectively, values in the low part of the ranges generally reported for these metals; no other direct measurements of metal content were attempted, but these two suggest that there has been little contamination of the water beyond slight dilution. One series of experiments was run on water acidified with HNO_3 immediately after collection, in order to prevent adsorption of ions or organic matter on the glass walls of the containing vessel. Comparison of results obtained in sea-water of various kinds — artificial sea-water, fresh natural sea-water which had stood in a soft-glass container for several weeks, and natural sea-water treated with HNO_3 — showed no differences in results greater than a factor of 2, which is within the accuracy attempted; hence for most experiments natural sea-water was used directly.

Thirteen metals were used in the experiments: Cu, Zn, Pb, Cd, Hg, Ag, Co, Ni, Bi, Mo, W, Cr, V. The metals were chosen primarily on the basis of ease of analysis. Many runs of several days' duration were necessary for each metal, and complicated analyses would have prolonged the work unduly. The group selected is a representative sample from the middle parts of the long series of the periodic system; it is hoped that the work can be extended to metals on either side, such as Ba, Sb, Se, and the rare-earth metals.

Results of the experiments are given in the third column of Table 3. The two figures listed for most of the metals show the concentrations obtained in approaching the solubility equilibrium from different directions. The wide gap between the figures for some of the metals is unexplained. Comparison of the second, third, and fourth columns of Table 3 shows that the measured equilibrium concentrations are uniformly larger than observed concentrations in sea-water, but have the same order of magnitude as the calculated concentrations (except Co). Some of the agreement with the calculated figures may be fortuitous; it certainly is in the case of copper, since the compound formed on adding Cu^{++} to sea-water is a basic chloride or a basic carbonate rather than the normal carbonate (HARVEY, 1945, p. 33). Nevertheless, the agreement is as close as could be expected in view of the assumptions underlying the calculations, and hence gives some basis for relying on these assumptions.

Only two figures have been found in the literature which can serve as checks on the measurements of equilibrium concentration. One is HARVEY's (1945, p. 33) statement that the amount of copper remaining in sea-water of pH 8 after a precipitate (basic chloride changing to basic carbonate) has been formed by the addition of CuSO_4 is 0.18 p.p.m. This is somewhat lower than the range (0.4–0.8) obtained in the present experiments. The second previously reported figure is SHIBASAKI's (1952) measurement of the copper remaining in solution after addition of CuSO_4 —1.9 p.p.m. (average of 1.65 and 2.1) at a pH of 7. SHIBASAKI's data do not permit a reliable extrapolation to pH 8, but his measurements at the

lower pH agree fairly well with the result of similar experiments described in the next section—2.5 p.p.m.

The ratios between experimental concentrations and those observed in sea-water are listed in the last column of Table 3. For four metals (Cu, Zn, Bi, Pb) the ratio is in the neighbourhood of 100, for all others (excluding the alkaline earths) greater than 1000. The uniformly high values corroborate the conclusion of the last section that the concentrations of these metals in aerated moderately warm sea-water cannot be controlled by solubility equilibria with ions ordinarily present in such water.

EFFECT OF TEMPERATURE, PRESSURE, AND pH

The experiments just described were conducted at room temperature (18°–23°C) and at the normal pH of sea-water (7.8–8.2). Equilibrium concentrations would of course be different in parts of the sea with different temperatures, pressures, and pH's and conceivably the difference might be sufficient for the concentrations to be reduced locally to the values actually observed. Then if circulation in the oceans is sufficiently rapid, the precipitation of rare metals in such local areas might control concentrations elsewhere—just as calcium in the sea is probably controlled by the formation of CaCO_3 in shallow tropical water, and phosphorus is probably controlled by the precipitation of carbonate-fluorapatite in areas of upwelling currents.

Calculation shows that an increase of one pH unit should diminish the solubility of simple divalent carbonates by a factor of 10, and that of divalent hydroxides by a factor of 100; these are the maximum expectable effects of pH changes. The effect of temperature is less easily calculated, but a survey of tabulated solubilities shows very few salts (and these unusual ones) whose solubility changes by a factor of more than 100 for a temperature change of 100°C; hence the effect of temperature in the range found in sea-water will be relatively slight. A change in pressure, according to the study of OWEN and BRINKLEY (1941), should also have little effect. Thus theoretically the four metals with the smallest ratios in Table 4 (Cu, Zn, Pb, Bi), provided that their precipitates are basic salts, and provided that the temperature effect aids the pH effect, might just possibly have their equilibrium concentrations reduced to the neighbourhood of the observed ones by a pH of 9, the maximum figure expectable in the sea.

To test this deduction, equilibrium concentrations of copper were measured at pH's of 7, 9, and 10 and at temperatures of 0° and 55°C (Table 5). The concentration decreases by a factor of about 4 for each unit increase in pH, and by a factor of about 2 for each 20° rise in temperature at pH 8 (why the change with pH should be so small is not obvious; theoretically it should be greater for either a basic chloride or a basic carbonate). Hence the concentration would be lowered on the order of 100 times at a pH of 10 and a temperature of 60°C—but these are impossibly high values for natural sea-water. Tests were not run on Zn, Pb, or Bi, but the results for Cu together with the theoretical deductions make it most unlikely that pH and temperature extremes in the sea are responsible for the observed concentrations. Such effects would be even less capable of controlling the concentrations of the other nine elements studied.

Table 5. *Equilibrium concentrations of copper as a function of temperature and pH*

	pH = 7 (p.p.m.)	pH = 8 (p.p.m.)	pH = 9 (p.p.m.)	pH = 10 (p.p.m.)
0°C		1.1		
18–20°	2.5	0.65	0.17	0.03
ca. 55°		0.15		

Solutions allowed to stand one day in contact with copper precipitate. Solutions with different pH's kept in tightly corked flasks; frequent adjustments of pH necessary because of exchange of CO₂ with the atmosphere at pH's different from 8.

PRECIPITATION OF SULPHIDES

Up to this point only aerated sea-water has been considered. This includes by far the greater part of the water in the oceans, for circulation is effective enough to keep an excess of dissolved oxygen even in water at great depths. In some parts of the ocean, however, notably in stagnant basins, in areas of upwelling currents, and in some of the bottom sediments, the water is depleted of its oxygen by decaying organic matter, and the chemical environment becomes reducing rather than oxidizing. Under such conditions two additional factors may affect rare-metal concentrations: the presence of sulphide ion, which is capable of forming very insoluble sulphides with some metals; and the presence of reducing agents powerful enough to change the valence of some metals and so to make possible other kinds of precipitation reactions. If sea-water circulates fast enough, the reduction of metal ion concentrations by these factors locally might be sufficient to maintain the low observed metal concentrations in the sea (W. W. RUBEY, personal communication).

To test this possibility, solubilities in sea-water of sulphide precipitates of several of the thirteen metals were measured (Table 6). Conditions roughly duplicated those of the most stagnant water found by STRØM (1936) in his study of Norwegian fjords—pH about 7 and H₂S concentration about 0.005M. As before, the measurements were made by approaching equilibrium from two directions—adding H₂S to solutions of each metal ion in sea-water, and placing the freshly precipitated metal sulphide in contact with sea-water. Again only rough values bracketed between maxima and minima could be obtained, but they are accurate enough for the purpose. Calculated concentrations for the experimental conditions—using KOLTHOFF and SANDELL'S (1952, p. 68) figures for the solubility products and multiplying by a correction factor for ionic strength—are given in the second column of Table 6.

For ZnS, both calculation and experiment show a concentration comparable with that found in nature. For Cu, Pb, Hg, and Ag the experimental concentrations are below the limit of detection by the analytical methods used, but the maximum possible concentrations differ from concentrations in the sea only by factors of 2–20; the calculated concentrations for these metals are much lower than concentrations in the sea. No tests were made on Cd or Bi, but results would doubtless be

Table 6. Calculated and measured concentrations of metals in equilibrium with HS^- and S^{--}

Metal	Concentration in equilibrium with HS^- and S^{--}		Concentration in sea-water (p.p.m.)
	Calculated (p.p.m.)	Measured (p.p.m.)	
Zn	0.02	0.008–0.07	0.005–0.021
Cu	7×10^{-14}	<0.003	0.001–0.015
Pb	0.0006	<0.02	0.003–0.008
Bi	6×10^{-18}	no data	0.0002
Cd	0.0002	no data	$32\text{--}75 \times 10^{-6}$
Ni	0.002	0.06–0.2	0.0001–0.0005 (0.0015–0.006)
Co	0.003	0.02–0.6	0.0001
Hg	2×10^{-29}	<0.005	0.00003
Ag	3×10^{-11}	<0.006	0.00015–0.0003
Cr	$10^{-34}?$	<0.004	$4\text{--}7 \times 10^{-5}$ (0.001–0.0025)
Mo	0.002?	6	0.0003–0.0007 (0.012–0.016)
W	no data	large	0.0001
*V	0.03	1	0.0003 (0.0024–0.007)

Parentheses indicate data from BLACK and MITCHELL (1952).

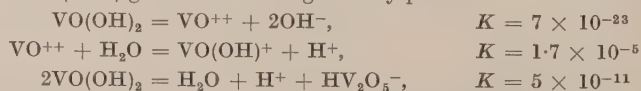
Calculated concentrations for Cr and Mo based on free-energy data from LATIMER (1952); for V on data from DUCRET (1951) and GARRELS (1953); others based on solubility products of the sulphides in KOLTHOFF and SANDELL (1952, p. 68).

Concentration of H_2S about 0.005M; pH ca. 7; temperature 18°–23°C.

* H_2S was added to solutions of both quadrivalent and quinquivalent vanadium. The resulting brownish-black precipitate appeared to be the same in each. Whether it is V_2S_3 , VS_2 , or a mixture (possibly with V_2S_5 also for VV) is uncertain. The equilibrium concentration of V in the solution was 1.0 p.p.m. for VIV and 1.3 p.p.m. for VV.

similar, since these metals also form very insoluble sulphides. The sulphides of Ni, Co, W, Mo, and V, on the other hand, are far too soluble to explain the concentrations of these metals. Chromium forms no sulphide in the presence of water, but H_2S slowly reduces chromate to the trivalent form, which precipitates as the hydroxide; and this reduces the amount of the metal below the concentration detectable colorimetrically. Hence the same conditions in the ocean that produce H_2S could control Cr by causing it to precipitate as the hydroxide.*

* A similar mechanism would be a possible control for vanadium, provided that the hydroxide or either the quadrivalent form, $\text{VO}(\text{OH})_2$, or the trivalent form, $\text{V}(\text{OH})_3$, is sufficiently insoluble. For quadrivalent V, DUCRET (1951) gives the following activity products:



from which it follows that the principal ion in equilibrium with $\text{VO}(\text{OH})_2$ at pH 7 is HV_2O_5^- , with a concentration of about $5 \times 10^{-4}\text{M}$, equivalent to 50 p.p.m. of V. Hence $\text{VO}(\text{OH})_2$ cannot possibly hold

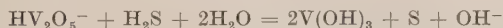
These data suggest that sulphide ion is a possible control for some of the metals. Against this conclusion is the fact that the concentrations of the metal ions have no apparent relation to the calculated solubilities of the sulphides; thus if Cu and Zn are both governed by the solubilities of their sulphides, the amount of Cu in sea-water should be a million million times smaller than the amount of Zn instead of almost equal to it. A possible answer to this objection is that the less soluble sulphides may form sulphide complexes, as has been demonstrated for Hg by TREADWELL and SCHAUFELBERGER (1946), for Ag by TREADWELL and HEPENSTRICK (1949), and for Pb by HEMLEY (1953).

To make this mechanism of control effective, it must be further demonstrated that sea-water circulation is rapid enough to bring all parts of the ocean in contact with H_2S at reasonably frequent intervals. Some light has been thrown on this question by the work of KULP (1951), whose measurements of the C^{14} content of ocean water from various depths indicate that circulation of large masses of water in the open sea is measured in thousands of years. This is probably fast enough for unusual conditions in local areas to exert a considerable influence on the ocean as a whole.

The rare metals which do not form very insoluble sulphides in sea-water (Ni, Co, Mo, W, V), and which therefore are not subject to direct control by sulphide ion, might still be removed from the sea in a sulphide-rich environment if they were appreciably coprecipitated with another sulphide. In order to test this possibility, experiments were tried in which ferrous sulphide (probably the most abundant sulphide formed in the sea) was precipitated in samples of sea-water to which solutions of each of the five metals had been added. Only vanadium, however, showed any lower concentration than would have been obtained by precipitating the metal sulphide without added iron. Even for vanadium the decrease is not large: the equilibrium concentration of either the quadrivalent or quinquevalent form is about 1 p.p.m. in the presence of vanadium sulphide alone, and 0.23 and 0.12 p.p.m. if iron sulphide is present also. Thus coprecipitation with ferrous sulphide can play little part in maintaining the low concentration of vanadium in sea-water, 0.0003 p.p.m.

To summarize, the precipitation of sulphides in local areas is a possible explanation for the observed low concentrations of Cu, Zn, Cd, Bi, Hg, Pb, Ag, and Cr in sea-water. The complete lack of parallelism, however, between sulphide solubilities and observed concentrations is not satisfactorily explained. For the metals V, Mo, W, Co, and Ni, equilibrium with sulphide ion cannot be responsible for observed concentrations.

the V concentration low enough, regardless of any equilibrium with H_2S . For $V(OH)_3$ the equilibrium to be considered is:



The free energy of formation of $HV_2O_5^-$ can be found from the first and third reactions above, together with LATIMER's figure of -109 kcal for VO^{++} ; it is approximately -357 kcal. GARRELS (1953) estimates -221 kcal as the free energy of formation of $V(OH)_3$. From these and the free energies for H_2S , H_2O and OH^- given by LATIMER, the standard free energy for the reaction turns out to be -2.4 kcal. For a pH of 7 and a concentration of H_2S 0.005M, this gives an equilibrium concentration of $HV_2O_5^-$ 3×10^{-7} M, or 0.03 p.p.m. of V. This figure is certainly a minimum, since it includes no correction for ionic strength or for possible complexes with other ions in sea-water; even so, it is 100 times greater than the usual figure for V in sea-water, 0.0003. It is 30 times smaller than the measured figure, 1 p.p.m., but such a discrepancy is expectable when ionic strength is not considered. Hence there seems to be no possibility experimentally or theoretically, that vanadium can be controlled by precipitation in a sulphide-rich environment.

ADSORPTION

General.—The efficacy of adsorption in controlling metal-ion concentrations is much more difficult to determine quantitatively than is the solubility of metal compounds. The amount of adsorption in any particular case depends not only on temperature, pH and salinity (as does solubility), but on time of standing, amount and physical state of the adsorbent, and concentration of the adsorbed ions as well. Despite the addition of these new variables to an already complex system, it seemed worth while to compare the effectiveness of different adsorbents on the various metal ions under similar conditions.

In some experiments the metal ion was removed from solution almost completely, whereas in others its concentration remained almost unaffected by the adsorbent. The question then arises: how effective must adsorption appear in such experiments to indicate large-scale removal of a metal from the sea? Obviously, even moderate adsorption repeated often enough as the ocean circulates could ultimately reduce the concentration of an adsorbed ion to a very small figure. Although the question cannot be answered completely with present data, one circumstance indicates that more than moderate adsorption is required. When zinc, for example, is adsorbed on montmorillonite from a 2-p.p.m. solution, some 99 per cent of the ion is removed within a few hours, whereas only about 20 per cent of silver ion is removed under the same conditions. Now if the adsorptive process in sea-water is equivalent to many repetitions of the laboratory process, as it would have to be in order to control the concentration of Ag^+ , the concentration of Zn^{++} would at the same time be lowered far below the observed amount in the sea. Hence the fact that zinc can be reduced almost to the concentration in nature by a single adsorption experiment with montmorillonite suggests that ions not so effectively removed in the laboratory are also less effectively controlled by adsorption on this material in the sea. It is on this basis that the laboratory experiments are considered to have at least a qualitative application to natural conditions.

Previous work.—Some recent experimental and theoretical work by KURBATOV, WOOD, and KURBATOV (1951), on the adsorption of cobalt by iron oxide, provides an excellent background for this discussion. These authors employed a radioactive tracer technique to analyse for cobalt, which enabled them to work with concentrations 1000 times lower than those used in the present experiments. Equilibrium in the adsorption process was reached within twenty-four hours when iron oxide was precipitated in a solution containing cobalt; when iron oxide was not precipitated in the same solution but added from the outside, the same equilibrium was eventually reached, but required six or seven days. In general, KUBATOV *et al.* found that adsorption increases with increasing amounts of adsorbent and adsorbate, with increasing pH, with decreasing temperature, and with decreasing concentrations of NH_4Cl . Log-log plots of cobalt adsorbed against cobalt in the original solution showed two regions: at low concentrations the graphs are straight lines, showing that the amount adsorbed is proportional to the concentration ("Henry's law region"), whereas at higher concentrations the relative amount adsorbed falls off. The position of the break in the curve depends on the conditions of the experiment, particularly on the amount of adsorbent. The experimental conditions were not exactly comparable to those of the present work, but enough

data are given to permit extrapolation; values so obtained are in satisfactory agreement with results of the present study.

KURBATOV *et al.* go on to show that their experimental results can be explained by a simple adsorption mechanism following a mass-law equation, the Co ions taking the place of H ions on the surface of the adsorbent. From the mass-law expression the following equation is derived:

$$\frac{y}{1-y} \cdot \frac{(H^+)^x}{(\text{amt. of adsorbent})^x} = K$$

in which y is the fraction of cobalt adsorbed, $1-y$ is the fraction left in solution, and x is an empirical constant. For the Henry's law part of the adsorption curves $y/(1-y)$ is constant as the total cobalt changes; above this part of the curve the amount of adsorbent left is significantly affected by the amount of Co, so that the value of the fraction falls off. The constant x has a value of 1.2 for cobalt, and plays the role of an "effective valence," indicating that the cobalt is present in solution partly as Co^{++} and partly as CoCl^+ or $\text{Co}(\text{OH})^+$. The role of NH_4Cl in decreasing the amount of adsorption is not described by the above equation, but is attributed by KURBATOV *et al.* to interference by Cl^- in the adsorption of Co.

In a later paper, DUVAL and KURBATOV (1952) compare the adsorption of barium and cobalt on ferric oxide. Barium shows a markedly smaller adsorption than cobalt, which the authors explain by the greater hydrolysis of Co^{++} .

One other set of experiments has a bearing on the present work. CORRENS (1924) determined the adsorption on kaolin of copper out of very dilute CuSO_4 solutions, and of lead out of $\text{Pb}(\text{NO}_3)_2$ solutions. The concentrations of metal ions used by CORRENS were similar to those in the present experiments, but other conditions were markedly different: the pH was lower, the amounts of adsorbent and of other ions in solution were smaller, and kaolinite was used instead of montmorillonite. These differences are ample explanation for the fact that CORRENS obtained much smaller values for the amounts of copper and lead adsorbed. CORRENS found that adsorption of the two ions was roughly similar, in agreement with the present work; his data for low concentrations of copper (0.1–0.5 p.p.m.) permit calculation of the quotient $y/(1-y)$, which is approximately constant in agreement with KURBATOV's results.

Experimental details. The present experiments are crude in comparison with the careful work of KURBATOV *et al.*, and have only the virtue of permitting many ions and several different adsorbents to be tested within a reasonable time. Amounts of a metal ion were added to samples of sea-water (usually 25 or 50 ml) to give concentrations in the range 0.1–10 p.p.m; then a measured amount of adsorbent was added (or precipitated), and the mixtures were shaken; at various times thereafter, up to a few days for most experiments, samples of the supernatant liquids were pipetted out and analysed colorimetrically. The pH was adjusted to 8.0–8.2 after addition of the metal ion and also after addition of the adsorbent; in some experiments repeated adjustments of pH were necessary while the adsorption was coming to equilibrium. Filtering was sometimes required to obtain samples for analysis free from particles of the adsorbent. The temperature ranged from 18° to 23°C. Blank tests were made to determine the amount of adsorption on glass and filter paper, and also to make sure that the colorimetric tests were not affected by the presence of the various adsorbents. Blank corrections were occasionally necessary, but they were never large.

Adsorbents were chosen to duplicate as closely as possible the principal adsorbing materials in the sea: iron oxide, manganese oxide, carbonate-fluorapatite, clay, and organic material. Other substances such as colloidal silica and calcium carbonate might have been added to the list, but the small concentrations of rare metals in silica and carbonate sediments is an indication that adsorption on these would be relatively minor. The degree of correspondence between the laboratory adsorbents and those in nature is of course open to question. In nature the adsorbents are doubtless formed by different processes, and their concentrations are generally less than in the experiments. Furthermore, the far longer times available for adsorption processes in nature perhaps make possible slow reactions which would not be detected in the laboratory. Despite these obvious shortcomings of the experiments, the laboratory work should provide in a general exploratory way some indication of what behaviour is to be expected from various ions and various adsorbents in the sea.

Ferric oxide, manganese dioxide, and apatite in most of the experiments were precipitated in the sample itself rather than added from outside. Ferric oxide was obtained simply by adding 0.1M FeCl_3 in small amounts, and adjusting the pH to 8.2 with NaOH solution after each addition. Apatite was precipitated by adding Na_2HPO_4 solution (containing 0.01 g P_2O_5 per ml), and again adjusting the pH at frequent intervals. Manganese dioxide was formed by adding 0.1M MnSO_4 and a slight excess of bromine water, then removing excess bromine by bubbling air through the solution and adjusting the pH. This procedure could not be used for Ni and Co because the divalent ions may be partly oxidized by free bromine, so MnO_2 was precipitated in sea-water in a separate flask, the bromine was bubbled out, and the suspension was added to sea-water containing the ion to be tested. Runs made with ferric oxide added from outside rather than precipitated verified the conclusion of KURBATOV *et al.* that the adsorptive capacity is the same but that a longer time is needed for adsorption equilibrium to be reached.

For clay, two samples of montmorillonite (bentonite) were used, one from Coalinga, California, and the other from Kinnekulle, Sweden. Montmorillonite was selected not because it is especially typical of marine environments, but because it should show the maximum adsorptive effect of which clay minerals are capable. Before use, both samples were washed with artificial sea-water until the wash water failed to give tests for the metals under investigation.

Two kinds of organic matter were tried: ordinary commercial peat-moss, and dead plankton suspended in sea-water obtained from the Oslo Fjord through the courtesy of Professor BJØRN FØYEN. One, it was hoped, would simulate terrestrial organic matter carried into the sea by streams, and the other would represent a common type of organic matter produced in the sea itself. Probably neither is very similar to the actual organic material with which the ions of sea-water are usually in contact, and experiments with them can serve only to give a rough idea of the efficacy of organic substances as adsorbents. The plankton was used without treatment, since the sea-water in contact with it showed no unusual concentration of metals; the peat-moss was washed with artificial sea-water until the wash water was free of rare metals.

Results.—Results of the adsorption experiments are shown in Table 7. The last column of the table gives for each run the per cent of the metal adsorbed, i.e., the difference between the numbers in the fifth and sixth columns divided by the number in the fifth column. The striking difference between adsorbabilities of some of the ions is shown, for example, by comparison of the figures for copper and silver; the dependence of adsorption on concentrations of adsorbent and adsorbate is particularly well shown by the data for cobalt and ferric oxide; the attainment of adsorption equilibrium in one or two days is illustrated by many of the runs, although the behaviour of mercury is an outstanding exception.

The data of Table 7 are obviously incomplete, and some of the figures are not as self-consistent as could be desired. The discrepancies arise in part from failure to keep temperature, pH, and concentrations strictly uniform, and in part from the fact that experimental objectives and methods changed as the work progressed, so that earlier data are not entirely comparable with later data. The results could

Table 7. Adsorption experiments (Temperature 18°–23°C, pH 7.7–8.2)

Adsorbent	Concentration of adsorbent (g/litre)	Volume of solution (ml)	Time (days)	Concentration of adsorbate		Percent adsorbed
				Initial (p.p.m.)	Final (p.p.m.)	
<i>Zinc</i>						
Fe ₂ O ₃ · nH ₂ O	0.03	25	1	2.0	0.1	95*
	0.03	25	8	2.0	0.15	93
Apatite	0.1	25	1	2.0	0.28	86*
	0.5	20	1	2.0	0.03	99
Clay	20	50	3	2.0	0.02	99*
Plankton	dilute	40	2	0.99	0.59	40*
	concd.	40	2	0.50	0.26	48*
Peat-moss	20	50	3	2.0	0.01	99*
<i>Copper</i>						
Fe ₂ O ₃ · nH ₂ O	0.03	25	2	0.65	0.014	98
	0.03	25	13	0.65	0.024	96
	0.03	25	14	0.65	0.025	96*
MnO ₂ · nH ₂ O	0.1	50	7	0.65	0.028	96*
Apatite	0.1	25	1	0.65	0.25	62
	0.1	25	6	0.65	0.15	77*
	0.5	20	1	0.65	0.015	98
Clay	15	20	1	0.65	0.07	89
	15	20	2	0.65	0.04	94*
Plankton	dilute	40	4	0.65	0.38	42
	concd.	40	6	0.65	0.30	54*
<i>Lead</i>						
Fe ₂ O ₃ · nH ₂ O	0.03	25	2	0.5	0.07	86*
Apatite	0.1	25	1	0.5	0.05	90
	0.1	25	6	0.5	0.02	96*
Clay	20	50	3	0.5	<0.02	>96*
Peat-moss	20	50	3	0.5	<0.02	>96*
<i>Nickel</i>						
Fe ₂ O ₃ · nH ₂ O	0.03	25	1	2.0	1.5	25
	0.03	25	9	2.0	1.35	33*
	0.3	50	2	1.92	0.12	94*
	0.3	50	2	0.49	0.033	93
	0.3	50	2	0.095	c. 0.01	c. 90

Table 7 (continued)

Adsorbent	Concentration of adsorbent (g/litre)	Volume of solution (ml)	Time (days)	Concentration of adsorbate		Percent adsorbed
				Initial (p.p.m.)	Final (p.p.m.)	
<i>Nickel</i>						
MnO ₂ · nH ₂ O	0.1	50	6	1.95	0.01	99*
	0.1	50	6	0.5	c. 0.002	c. 99
Apatite	0.1	25	2	2.0	1.9	5
	0.1	25	6	2.0	1.85	8*
	0.5	20	1	2.0	1.35	33
	0.7	50	2	0.19	0.06	69*
	0.7	50	7	0.19	0.06	69
Clay	12	25	2	2.0	1.8	10*
Plankton	dilute	40	8	1.95	c. 1.8	c. 8
	dilute	40	14	1.95	1.8	8*
<i>Cobalt</i>						
Fe ₂ O ₃ · nH ₂ O	0.3	50	3	1.92	0.22	89
	0.3	50	3	0.49	0.055	91*
	0.3	50	3	0.1	c. 0.01	c. 90
	0.03	50	3	1.92	1.25	35*
	0.03	50	3	0.49	0.27	45
	0.03	50	3	0.1	0.035	65
	0.003	50	3	0.1	0.07	30
	0.03	25	1	2.0	1.4	30
	0.03	25	9	2.0	1.6?	20?
MnO ₂ · nH ₂ O	0.1	50	5	1.95	0.13	93*
	0.1	50	5	0.5	0.031	94*
Apatite	0.1	25	2	2.0	1.7	15*
	0.5	20	1	2.0	0.8	60
	0.7	50	9	0.19	0.035	82*
Clay	12	25	2	2.0	1.65	18*
Plankton	dilute	40	3	1.95	1.6	18
	dilute	40	15	1.95	1.8	8*
<i>Mercury^{II}</i>						
Fe ₂ O ₃ · nH ₂ O	0.3	50	3	1.9	1.7	10
	0.3	50	9	1.9	1.9	<5
	0.3	50	12	1.9	1.9	<5
	0.3	50	16	1.9	1.5	20
	0.3	50	9	0.2	0.18	10
	0.3	50	12	0.2	0.1	50
	0.3	50	16	0.2	0.06	70

Table 7 (continued)

Adsorbent	Concentration of adsorbent (g/litre)	Volume of solution (ml)	Time (days)	Concentration of adsorbate		Percent adsorbed
				Initial (p.p.m.)	Final (p.p.m.)	
<i>Mercury</i> ^{II}						
Fe ₂ O ₃ · nH ₂ O	0.03	50	3	1.95	1.85	5
	0.03	50	9	1.95	1.95	<5
	0.03	50	12	1.95	2.1	<5
	0.03	50	16	1.95	0.9	50*
	0.03	50	2	0.2	0.19	5
	0.03	50	6	0.2	0.02	90
	0.03	50	9	0.2	<0.04	>80
	0.03	50	12	0.2	<0.01	>95*
Apatite	0.5	50	3	1.9	1.9	<5
	0.5	50	9	1.9	2.0	<5*
	0.5	50	9	0.2	0.15	25*
Clay	7	50	3	1.95	1.8	8
	7	50	9	1.95	0.08	96*
	7	50	9	0.2	<0.02	>90
	20	50	3	2.0	1.2	40
	20	50	25	2.0	0.2	90
Plankton	dilute	40	3	2.4	0.08	98*
Peat-moss	20	50	4	4	0.05	99*
<i>Silver</i>						
Fe ₂ O ₃ · nH ₂ O	0.3	50	3	1.92	1.50	22*
	0.3	50	3	0.59	0.50	15
	0.3	50	3	0.20	0.16	20*
	0.03	25	2	2.2	1.2	45?
	0.03	25	13	2.2	1.3	41?
MnO ₂ · nH ₂ O	0.1	50	7	0.5	0.46	8*
Apatite	0.1	25	1	2.0	1.1	45?
	0.1	25	6	2.0	1.55	23*
	0.5	20	1	2.0	1.3	35
	0.7	50	2	0.48	0.45	6*
Clay	20	50	4	1.0	0.8	20*
Plankton	dilute	40	8	1.95	1.00	49*
	concd.	40	2	0.49	0.02	96*
Peat-moss	20	50	4	1.0	0.46	54*

Table 7 (continued)

Adsorbent	Concentration of adsorbent (g/litre)	Volume of solution (ml)	Time (days)	Concentration of adsorbate		Percent adsorbed
				Initial (p.p.m.)	Final (p.p.m.)	
<i>Chromium^{VI}</i>						
Fe ₂ O ₃ · nH ₂ O	0.3	50	2	1.94	1.71	12*
	0.3	50	2	0.49	0.38	22
	0.3	50	2	0.095	0.050	47
	0.3	50	9	1.94	1.75	10*
	0.3	50	9	0.49	0.38	16
	0.3	50	9	0.095	0.048	49*
	0.04	20	2	10	c. 7	c. 30?
	1.0	15	1	10	c. 6	c. 40?
MnO ₂ · nH ₂ O	0.1	50	4	1.75	0.13	94*†
	0.1	50	4	0.5	0.05	90
	0.1	50	8	0.5	0.055	89
Apatite	0.1	25	2	4	3.5	12*
	0.1	25	6	4	3.5	12
	0.5	20	2	4	3.4	15
Clay	12	25	3	4	3.7	8
Plankton	dilute	40	7	1.95	1.71	12
	dilute	40	14	1.95	1.75	10*
<i>Molybdenum</i>						
Fe ₂ O ₃ · nH ₂ O	0.3	50	2	4.7	2.9	38
	0.3	50	2	1.45	0.66	54
	0.3	50	2	0.39	0.16	59
	0.3	50	7	4.7	3.0	36
	0.3	50	7	1.45	0.8	45
	0.3	50	7	0.39	0.17	56*
	0.03	25	2	4	3	25*
	0.03	25	12	4	4	<5?
	1.0	15	1	1.0	0.35	65?
MnO ₂ · nH ₂ O	0.1	50	3	1.95	1.7	13
	0.1	50	3	0.5	0.45	10
	0.1	50	8	1.95	1.7	13
	0.1	50	8	0.5	0.13	74?*
	0.02	50	1	4	2	50*
	0.2	50	1	1.0	0.2	80?†
Apatite	0.1	25	2	4	3.6	10*
	0.5	20	2	4	3.2	20
Clay	20	50	4	2	1.3	35*
	20	50	4	8	6	25

Table 7 (continued)

Adsorbent	Concentration of adsorbent (g/litre)	Volume of solution (ml)	Time (days)	Concentration of adsorbate		Percent adsorbed
				Initial (p.p.m.)	Final (p.p.m.)	
<i>Molybdenum</i>						
Plankton	dilute	40	4	1.95	1.65	15*
Peat-moss	20	50	4	8	c. 3.8	c. 53?*
<i>Tungsten</i>						
$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	0.03	25	2	8	1.6	80*
	0.03	25	9	8	1.8	78
	0.03	25	12	8	1.1	86
$\text{MnO}_2 \cdot n\text{H}_2\text{O}$	0.02	25	2	4	0.05	99*
Apatite	0.1	25	2	4	4	<2
	0.5	20	2	4	3.8	5*
Plankton	dilute	40	7	1.95	c. 1.8	c. 8*
<i>Vanadium</i> ^{IV}						
$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	0.03	25	2	2.6	0.2	92
	0.03	25	9	2.6	0.1	>96*
Apatite	0.1	25	2	2.6	2.5	4
	0.5	20	1	2.6	2.1	19*
Clay	12	25	2	2.6	1.9	27*
Plankton	dilute	40	6	2.5	2.1	16*
	dilute	40	17	2.5	2.2	12
<i>Vanadium</i> ^V						
$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	0.03	25	1	4	0.8	80
	0.03	25	5	4	0.2	95*
$\text{MnO}_2 \cdot n\text{H}_2\text{O}$	0.1	50	7	0.5	0.3	40*
	0.03	50	4	4	3.1	23*
Apatite	0.1	25	2	4	3.3	17*
	0.1	25	6	4	3.8	5
	0.5	20	1	4	2.8	30
Clay	12	25	2	4	2.7	33*
Plankton	dilute	40	6	1.93	1.78	8?
	dilute	40	17	1.93	2.0	<3*
	dilute	40	11	0.81	0.85	<3

Asterisks designate numbers repeated in Table 8. Question marks indicate values which seem markedly inconsistent with other data; some of these are older results obtained before the analytical methods had been fully explored. Daggers indicate two runs in which the pH dropped to 7.3 before the analysis was made.

certainly be made more presentable by repeating the earlier experiments, using procedures adopted toward the end, and by making additional measurements to fill gaps in the table. The effort hardly seemed justified in view of the facts that the theoretical basis for comparing one element with another is uncertain, that correspondence with actual conditions in the sea is not very close, and that complete reproducibility was not attained even in runs carried out with meticulous care to insure constant conditions. The experiments, be it repeated once more, were intended only to provide gross comparisons between different metals, and for this purpose the data seem accurate enough.

Significant relationships among the various adsorbents and adsorbates are not well displayed in Table 7. Some selection of data for comparison is clearly needed, and several possibilities suggest themselves. One may choose figures obtained with similar initial concentrations of metal ions and similar amounts of the different adsorbents; or one may pick figures corresponding to similar final concentrations of the different metals left in solution when adsorption has reached equilibrium; or (following KURBATOV *et al.*) one may try to establish a "Henry's law" part of the adsorption curve for each metal, and then compare values of $y/(1-y)$. Which procedure theoretically will give the most meaningful comparison is not immediately obvious, but with present data the first procedure proves to be the only feasible one. The third procedure is ruled out because for several of the metals a constant $y/(1-y)$ could be reached only at dilutions inaccessible to the simple methods of analysis employed. The second procedure is not applicable to as many of the data as is the first, and results of using it where possible show that in any event the relations obtained would not be very different. The selection of data according to the first procedure, i.e., for similar initial concentrations of adsorbents and adsorbates, leads to the compilation in Table 8.

In this table each adsorbent-adsorbate combination is represented by a single number, or at most a pair of numbers. The numbers selected (indicated by asterisks in Table 7) are in general maximum values obtained for the combination of concentrations used, except where a lower value was clearly the more trustworthy experimental result. Parentheses indicate values obtained for lower concentrations of adsorbate, and underlining denotes higher concentrations of adsorbent. The numbers in Table 8 obviously have little quantitative meaning, but provide a basis for rough qualitative comparisons.

Discussion.—Copper, zinc, and lead, according to Table 8, are adsorbed more strongly and more consistently than the other metals. All the adsorbents except plankton reduce the concentrations of these three within a few hours nearly to the range found in sea-water. Cobalt and nickel, although likewise divalent elements, are much less effectively adsorbed. For these two metals manganese dioxide is by far the best adsorbent; adsorption on other materials can be greatly increased by increasing the amount of adsorbent and reducing the concentration of the metal ions, as is shown by the figures in parentheses. Mercury shows the greatest adsorption on plankton of any metal, and it shows strong adsorption by montmorillonite, but notably weak adsorption by apatite; its behaviour is peculiar in that adsorption equilibrium is apparently reached only slowly, especially with iron oxide and clay (Table 7). Silver is surprisingly little affected by any

of the adsorbents except organic materials, even in dilute solutions containing large amounts of adsorbent. Chromium and tungsten are adsorbed readily by manganese dioxide, molybdenum somewhat less so; tungsten shows moderate adsorption by iron oxide, chromium and molybdenum very little. In contrast to these three, vanadium is adsorbed much more strongly by iron oxide than by manganese oxide; other adsorbents affect it only slightly.

Table 8. Summary of results of absorption experiments

<i>Metal</i>	<i>Hydrated Fe₂O₃</i>	<i>Hydrated MnO₂</i>	<i>Apatite</i>	<i>Clay</i>	<i>Plankton</i>	<i>Peat- moss</i>
Zn	95		86	99	40 (48)	99
Cu	96	96	77	94	54	
Pb	86		96	>96		>96
Ni	33 (94)	99	8 (69)	10	8	
Co	35 (91)	93 (94)	15 (82)	18	8	
Hg	50 (>95)		<5 (25)	96	98	99
Ag	22 (20)	(8)	23 (6)	20	49 (96)	54
Cr	10 (49)	94	12	8	10	
Mo	25 (56)	50 (74?)	10	35	15	53?
W	80	99	5		c. 8	
V ^{IV}	>96		19	27	16	
V ^V	95	23 (40)	17	33	<3	

Concentration of adsorbate: 0.6–2.5 p.p.m. for first seven elements, 2–10 p.p.m. for last five. A second number in parentheses is the percent adsorption for lower concentrations of adsorbate, in the range 0.1–0.7 p.p.m.

Concentrations of adsorbent: for Fe₂O₃, MnO₂, and apatite, 0.02–0.1 gram/litre, except for *underlined* figures, which have 0.3–0.7 gram/litre; for clay and peat-moss, 7–20 gram/litre; for plankton, not measured.

All values are given as percent of metal adsorbed. Figures are the same as figures marked with an asterisk in Table 7.

Temperature 18°–23°C, pH 7.7–8.2.

Of the various adsorbents, manganese dioxide appears to be most effective and iron oxide next. The other adsorbents are relatively inactive unless they are present in large amounts, except toward Cu, Zn, Pb, and Hg.

The tables show little apparent correlation between the adsorptive behaviour of the metals and their other chemical properties. Colloidal manganese dioxide is commonly thought to carry a negative charge and hence to attract cations, whereas colloidal iron oxide normally has a positive charge and should attract anions. In the tables, however, the anion-forming elements Cr and W are as effectively adsorbed by manganese dioxide as are the cation-forming elements Ni and Co. These results provide no explanation for GOLDBERG's (1954) conclusion that, in manganese nodules, Co is concentrated with iron, and Ni and Cu with manganese. The markedly smaller adsorption of Ni and Co as compared with Cu, Zn, and Pb, despite the similarity of their ions in sea-water, may possibly be correlated with the greater polarizing ability (greater chalcophile tendency)

of elements with complete 18-electron shells. The very weak adsorption of Ag and V by most of the materials used may be connected with the fact that they form univalent anions.

The elements Bi and Cd were not studied in this part of the work because of analytical difficulties with the small concentrations remaining after adsorption had taken place. Both might be expected to behave like Cu, Zn, and Pb, as they are chalcophile elements existing in sea-water partly as positive ions. The adsorption of Cd may be lessened by the fact that much of it in the sea would form neutral CdCl_2 molecules; the extent of adsorption of Bi is unpredictable, as the proportion of it in the form of undissociated BiOCl is not known.

ORGANIC PROCESSES

Another possible way in which metal concentrations may be controlled is by reactions in living organisms. If metals taken up in biologic processes are returned to the sea shortly after the death of the organism, the control will be only temporary; but the possibility remains that some metal-containing compounds may survive partial decay and burial of the organisms, and so may help to remove metals permanently from the sea. The well-known fact that rare metals are often notably enriched in organic sediments is an indication that this process may be of considerable importance.

To evaluate the role of organic processes even qualitatively seems all but impossible. A wealth of data exists on the rare-metal content of individual organisms (for a comprehensive tabulation see VINOGRADOV, 1953), but the content ranges so widely from species to species and from season to season that overall averages have little meaning. Even if such averages could be obtained, data are completely lacking on the relative importance of different organisms in the rare-metal economy of the sea and on the relative stabilities of metal-organic compounds. The problem can also be approached from the other end, by analyzing organic sediments for rare metals, but the obvious difficulty here is that an unknown fraction of the metal content owes its presence to adsorption and possibly to sulphide precipitation rather than to biologic reactions.

As examples to show how important the enrichment of rare metals in organisms can be, data from two recent detailed studies are brought together in Table 9. The second column shows enrichment factors (ratios of concentrations in organisms to concentrations in sea-water) obtained by BLACK and MITCHELL (1952) for brown algae, and the fourth column gives similar figures for nine representative animals analyzed by NODDACK and NODDACK (1939). Both of these investigations also include measurements of concentrations of the metals in sea-water; some of the figures obtained are widely different, so it seemed reasonable to include also enrichment factors recalculated with concentrations obtained by the other investigators (third and fifth columns). The high enrichment factors for some metals and the great diversity in values are especially notable. Tentatively one might conclude from the table that the six elements Ni, V, Zn, Cd, Co, and Ag show more enrichment in these particular organisms than do the other five elements listed, but this is hardly an adequate basis for assuming that such a relationship is universal among marine organisms.

Table 9. Representative data on concentrations of rare metals in marine organisms

<i>Metal</i>	<i>Enrichment factor for brown algae, fresh weight (data of BLACK and MITCHELL, 1952)</i>	<i>Same, using values of NODDACK and NODDACK (1939) for concentrations in sea-water</i>	<i>Average enrichment factor for 9 marine animals, dry weight (data of NODDACK and NODDACK, 1939)</i>	<i>Same, using values of BLACK and MITCHELL (1952) for concentrations in sea-water</i>
Ni	200–1,000	1,600–8,000	41,000	5,000
V	10–300	>160–5,000	>280,000	17,000
Zn	400–1,400	400–1,400	32,500	32,500
Mo	2–15	60–420	6,000	200
Cr	100–500	3,000–15,000 ^α	>1,400	200
Co	(>4,500)	(13,000)	21,000	>7,000
Ag	(10–>150)	(600)	22,000	1,000–>7,000
Pb	(>410)	(410)	2,600	2,600 ^β
Cu		(410)	7,500	2,600 ^β
Cd			>4,500	27,000–67,000 ^γ
Bi			1,000	1,000 ^β

^α Calculated from concentration in sea-water given by ISHIBASHI (1953).

^β Calculated from concentration in sea-water given by MASON (1952).

^γ Calculated from concentration in sea-water given by MULLIN and RILEY (1954).

Numbers in parentheses are not given explicitly by BLACK and MITCHELL, (1952) but are estimated from their data.

COMPARISON OF POSSIBLE CONTROL MECHANISMS

Three processes survive this inquiry into possible control mechanisms for rare-metal concentrations in sea-water. One is the precipitation of sulphides within bottom sediments or in isolated areas of reducing conditions, a second is adsorption, and the third is biologic processes. The relative effectiveness of the first two can be roughly evaluated from the experimental results; no pertinent data exist regarding the third, so that it can be safely assigned a primary role only for metals for which the first two processes are inadequate.

The precipitation of sulphides, as pointed out previously, can reduce the concentrations of eight of the thirteen elements under discussion to values within or lower than the ranges found in sea-water. As a major control of concentration, the mechanism is questionable, because observed concentrations bear no apparent relation to solubilities of the sulphides. The validity of this objection is not altogether certain, because the experimental work could not be carried to low enough concentrations, and because calculated solubilities may be modified by the formation of complex ions.

To evaluate adsorption processes as a control of concentrations requires a different basis of comparison. Adsorption processes, unlike precipitation processes, are cumulative; no matter how small the concentration of an ion may be, addition of fresh adsorbent will reduce it further. In other words, if addition of rare-metal ions to the sea were suddenly to cease altogether, an adsorption mechanism would ultimately lower metal-ion concentrations below any assigned limit, while

a precipitation process would maintain the concentrations at values fixed by the solubility products. This means that absolute values of the concentrations can give little information about the effectiveness of adsorption processes. A more significant measure would be the rate of removal of the various metals from the sea, which cannot itself be easily measured but which can be compared for different elements in an indirect way. The efficiency of removal of a metal is evidently related to (1) the steady-state concentration and to (2) the rate of supply. If the concentration is low with respect to the rate of supply, removal must be rapid; if the ratio of concentration to rate of supply is large, removal must be sluggish. These two factors, concentration and rate of supply, have already been listed in Table 1. The last column of this table, which shows ratios of concentration to supply, should be a measure of relative efficiencies of removal and hence of relative amounts of adsorption—provided that adsorption is indeed the controlling factor in determining concentrations.

To test the efficacy of adsorption processes, the percentages in Table 1 are now compared with predictions based on the experimental data of Table 8. Underlying such a comparison are several assumptions. With regard to Table 1, the chief assumptions are (1) the rate of supply of rare metals to the sea has been constant through geologic time, (2) rare metals go entirely into solution during weathering, and (3) the analytical data on rare-metal concentrations are reliable. None of these assumptions is strictly true, of course, but they are probably not so far wrong that they invalidate qualitative comparisons. Regarding Table 8, one must make some sort of guess as to the relative importance of the different adsorbents in the ocean. Presumably ferric oxide would play a greater role than manganese oxide, since more iron is brought to the sea than manganese; apatite probably has less effect than other adsorbents, since its amount in sediments is smaller; clay should be more important near the shore than far from shore. But such statements do not permit quantitative evaluation, so the simplest assumption will be used—that the adsorbents are of roughly equal importance, and that therefore an average of the figures for each element gives a crude measure of its adsorbability. A further convention is adopted, that adsorption in the more concentrated solutions (figures without parentheses in Table 8), amounting to 40 per cent or more, is considered “strong” adsorption.

The percentages in Table 1 divide the elements into three groups: those least effectively removed from sea-water, with percentages 0.2 and over (Ag, Bi); an intermediate group with percentages between 0.005 and 0.2 (Cd, Pb, Cu, Zn, Mo, Hg); and a group showing the most effective removal, with percentages less than 0.005 (Ni, Co, V, Cr, W).

The adsorption experiments give at once a basis for predicting the extent of removal of elements which are supplied to the sea in roughly equal amounts. Copper, zinc, and lead, for example, are probably added to the sea in about the same quantities and are all strongly adsorbed by several different materials, so that a general similarity in their ratios would be expected. On the other hand an element supplied in much smaller amounts might be removed to the same extent, even though its measured adsorbability is less, simply because the percentage adsorption increases as the concentration of metal decreases. Mercury, for example, shows

less net adsorption than Cu, Zn, and Pb at high concentrations, but shows comparable adsorption at low concentrations (Table 8), so that the similarity in percentages shown in Table 1 is understandable. The difficulty is that the effect of concentration on adsorbability is not quantitatively predictable with present data, so that agreement of the percentages may be fortuitous.

For molybdenum a similar explanation can be suggested, although it is less plausible, because molybdenum even at low concentrations is adsorbed much less than is mercury. The data of Table 8, in fact, suggest that removal of molybdenum should be scarcely more effective than that of silver. The data concerning molybdenum are so diverse, both with respect to its crustal abundance and to its concentration in sea-water (Table 1), that a satisfactory test of this prediction is impossible. The generally accepted concentration range would put the element in the group with Pb, Cu, and Zn; but the recent much higher figures given by BLACK and MITCHELL (1952) and by ISHIBASHI (1953) would place it ahead of silver.

For silver the agreement between prediction from Table 8 and data from Table 1 is excellent. It is the metal least subject to adsorption in the laboratory, and likewise the metal least effectively removed from the sea.

Bismuth and cadmium were not studied experimentally. For bismuth a guess may be hazarded that its relatively slight removal from sea-water is due to its probable existence as a univalent ion (BiO^+ or BiCl_4^-) and the undissociated molecule BiOCl , neither of which would be strongly adsorbed. Cadmium, by similar reasoning, should also be in the first group, as it would form chiefly CdCl^+ and CdCl_2 in sea-water; it is not seriously out of place, however, inasmuch as its ratio is next to the highest among the elements in the second group.

For the elements Ni, Co, V, W, and Cr, adsorption fails to provide a complete explanation. These metals are supplied to the sea in amounts comparable to those of Cu, Zn, and Pb (Table 1), and they are much less affected by most adsorbents (Table 8), yet their removal from sea-water is more effective by factors of 10–100. It is true that their adsorption increases with dilution, and that data were not obtained at concentrations close to those in natural sea-water; still it seems highly improbable that any adsorption process at lower concentrations would become *more* effective for those elements than for Cu, Zn, and Pb. Stated another way, any imagined adsorption process that could control the concentrations of Ni and Co should at the same time reduce the amounts of Cu and Zn far below their observed values.

The possible alternative control by precipitation in sulphide-rich environments is not feasible for Ni, Co, V, or W, but may account for removal of Cr. Not even sulphide is required for this element; any reducing environment capable of changing it to the trivalent form will cause its removal as the insoluble $\text{Cr}(\text{OH})_3$.

The very efficient removal of V, Ni, Co, and W from sea-water seems most plausibly explained by organic reactions. Admittedly this is a hypothesis justified principally by the failure of alternative hypotheses; yet there is some indirect evidence for such a mechanism, at least for V and Ni. These elements are usually the two that show greatest enrichment in organic sediments (e.g., GOLDSCHMIDT, KREJCI-GRAF, and WITTE, 1948; ERICKSON, MYERS, and HERR, 1954), and also are among those most strongly enriched in marine organisms (Table 9). Cobalt

is also prominent among the elements concentrated by organisms (Table 9), but its enrichment in organic sediments is less marked and less consistent than that of V and Ni. Tungsten has been noted as being present in marine organisms and in organic sediments, but nothing is known about its degree of enrichment in either; to ascribe its removal from the sea to organic agencies is accordingly a pure assumption.

In summary, adsorption provides the most satisfactory general explanation for the observed concentrations of rare-metal ions in the sea. It must be supplemented with biologic processes to account for the low concentrations of V and Ni, and probably also for Co and W. The small figure for Cr is most plausibly explained by reduction in parts of the sea where organic matter accumulates. Local precipitation of sulphides cannot be ruled out as a contributing factor, but it is certainly not the major control.

CORRELATION WITH RARE ELEMENTS IN MARINE SEDIMENTS

The mechanism controlling rare-metal concentrations in the sea should be reflected both in the abundance and in the mode of occurrence of the metals in various marine sedimentary rocks. Unfortunately, neither the data of this report nor existing data on rare-metal occurrences in sedimentary rocks (summarized in KRAUSKOPF, 1955) are sufficiently accurate or complete to make correlations more than tentative.

Although sulphide precipitation is a possible means of limiting the concentrations of Ag, Cu, Pb, Zn, Cd, and Hg, sulphides of these metals are not common in sedimentary rocks, nor are the metals notably concentrated in sedimentary pyrite. Even where the presence of rare-metal sulphides has been established in sediments, there is no assurance that the metals were originally deposited in this form. Hence evidence from sedimentary rocks does not support the hypothesis that insoluble sulphides are a controlling factor in the sea, but on the other hand the evidence offers no convincing disproof.

The adsorption experiments suggest that Cu, Zn, and Pb, which are strongly adsorbed by many different substances, should be widely distributed in minor amounts in marine sediments. Moderate concentrations of these elements might be expected in sediments deposited slowly, with little addition of coarse clastic material; large concentrations should be uncommon, but might be associated with various kinds of adsorbents in places where the local supply of metals was abnormally great. These predictions accord well with experience. Mercury and cadmium might well be included in this group, but too little is known about their occurrence to test the prediction. Silver, little affected by most adsorbents but strongly held by organic matter, would be expected in large amounts in carbonaceous sediments, which again corresponds with observation. The strong adsorption of Co and Ni on the hydrated oxides of iron and manganese is a convenient explanation for the frequent presence of these elements in iron and manganese ores. The observed concentration of V in sedimentary iron oxides and of Mo in manganese oxides agrees with the adsorption experiments. Data on rare-metal concentrations in marine hydroxide and oxide sediments are so fragmentary, however, that a satisfactory check against the experimental work is not possible.

Apatite precipitated from sea-water (Table 8) is not an effective adsorbent for the metals considered in this study, with the exception of the three (Cu, Zn, Pb), which are strongly adsorbed by all the other absorbents as well. Accordingly there is no reason to expect notable amounts of any of these metals to be found in phosphorites. In agreement with this prediction, analysis of existing data on phosphorites (KRAUSKOPF, 1955) shows that most of the metals sometimes enriched in these rocks owe their presence to organic matter rather than to apatite, and that the few metals which are associated with apatite itself are not among those included in this study.

Black shales and asphalts often contain, in addition to silver, notable concentrations of V, Ni, Mo, and Pb, and less commonly also Cu, Co, Zn, and Cr (also Au, As, and Sn, which are not under discussion here). The enrichment in V and Ni can be ascribed reasonably to their uptake in biologic reactions, as discussed in the preceding section. Cobalt can be explained in similar fashion, but less convincingly. Moderate enrichment of Pb, Zn, and Cu can be attributed to adsorption, if the carbonaceous sediments are assumed to represent unusually slow deposition; all three are also known to play specific roles in some organisms (NODDACK and NODDACK, 1939; MARKS, 1938). Local extremely large concentrations of these elements (as in the Kupferschiefer and occasional beds in the Phosphoria formation) are difficult to explain without some abnormality of supply. The presence of Cr in organic sediments is expectable because no process is known which might limit the concentration of this element except reduction to the trivalent state in environments where carbonaceous material would be deposited. A good reason for the great enrichment of Mo in black shales and asphalts is difficult to find; it is not conspicuously adsorbed by organic material, and seems to show only modest enrichment in marine organisms (Table 9). Despite the lack of confirmatory evidence, the enrichment of Mo is most plausibly ascribed to a biologic process.

It is worth emphasizing that four of the rare metals most characteristic of black shales and asphalts (V, Ni, Co, Mo) belong to the group which, according to the experiments, cannot possibly be controlled in sea-water by precipitation of sulphides. The first three are also in the group for which adsorption is an inadequate explanation, and are among the metals known to be greatly concentrated in some marine organisms. Such a combination of facts is difficult to explain without assuming that biologic processes play an important role in the enrichment of these metals in sedimentary rocks.

In summary, the conclusion from the experimental part of this work, that adsorption processes are the most important controls of rare-metal concentrations in the sea, is in general agreement with available data on the distribution of elements in sedimentary rocks of marine origin. But neither the data on distribution nor the experimental results are sufficiently accurate and inclusive to make the test of hypothesis against observation wholly convincing.

SUMMARY

Factors controlling the concentrations of Cu, Zn, Cd, Hg, Pb, Ag, Bi, Cr, Mo, W, Ni, Co, and V in the sea were studied. The principal conclusions are as follows:

1. The concentrations are not controlled by the low solubility of compounds

formed with the ions present in normal aerated sea-water; in other words, sea-water is far from saturated with any of these metals. This conclusion is suggested by calculations and confirmed by experiment.

2. Variations in the pH and temperature of sea-water affect the solubilities of rare-metal compounds locally, but in aerated sea-water the variations are not sufficient to make solubilities an effective control of concentration. In other words, aerated sea-water is unsaturated with respect to any of the thirteen metals even in places where the pH and temperature have extreme values.

3. In sea-water containing H_2S (and therefore depleted in oxygen), Zn is reduced to a concentration similar to that in nature, and the amounts of Cu, Pb, Hg, Ag, and Cr (probably also Bi and Cd) become too small to measure by simple methods. Amounts of these metals in the sea, therefore, could be controlled at least in part by the precipitation of sulphides locally in reducing environments, provided that circulation of ocean water is sufficiently rapid. (Chromium is not precipitated as a sulphide, but is reduced and precipitated as the hydroxide.) The concentrations of these metals, however, have no discernible relation to the solubilities of their sulphides, so that precipitation of sulphides is probably not a major controlling factor.

4. Sulphide precipitation cannot be a control for Co, Ni, Mo, W, or V. Even coprecipitation with FeS does not bring the concentration of these metals into the range found in sea-water.

5. Adsorption is a possible control for all the metals except V, Co, Ni, W, and Cr. Relative efficiencies of adsorption of the various metals are in rough agreement with observed rates of removal from the sea.

6. The metals V and Ni (possibly also Co, W, and Mo) are probably controlled largely by organic reactions. The control of Cr is most reasonably ascribed to local reduction and precipitation as $Cr(OH)_3$.

7. Of the various adsorbents in sea-water, hydrated manganese dioxide appears to be most efficient (weight for weight), and hydrated ferric oxide next. The three metals Cu, Zn, and Pb are strongly absorbed on all the adsorbents tried; other metals show marked differences in the effects of different adsorbents.

8. The occurrence of rare metals in marine sedimentary rocks is in rough agreement with predictions made from the hypothesis that metal concentrations in the sea are controlled chiefly by adsorption, supplemented by organic reactions and by precipitation in sulphide-rich environments.

These conclusions, established for thirteen elements only, can probably be extended to other metals in the central part of the periodic system, i.e., to those elements which have a complete or nearly complete 18-electron shell in their atoms and not more than five valence electrons outside this shell. To extend the conclusions to metals at the extremes of the system, such as Sr, Cs, Y, As, or Se, would be unwarranted.

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NOTE

Owing to the last minute withdrawal of a paper intended for this issue, the pagination runs 32, 32a and 32b.

This departure from journal style has been preferred to the alternative of reprinting and consequent long delay in publication. The publishers trust that this would be the wish of their readers.

Readers are requested to accept the apologies of the publishers and to grant their indulgence.

The geochemistry of some igneous rock series—III

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ABSTRACT

This paper deals with the distribution of some of the commoner trace elements with respect to the major elements in certain tholeiitic igneous rock series. These include series from the Hakone volcano and the adjacent area, from the Karroo dolerites, from the British Tertiary province, the Northfield sill, and the almost undifferentiated tholeiitic basalts of Hawaii and Oahu. A little data on the Satakunta dolerite hybrids is also provided.

INTRODUCTION

THIS, the third of our series of papers* concerning the behaviour of the commoner trace elements with respect to the major constituents in some well-known igneous rock series, investigates their behaviour in certain tholeiitic igneous rock series.

The method of investigation has been the same as that detailed in the first paper of this series (NOCKOLDS and ALLEN, 1953), and the diagrams presented here are all of the same form, and on the same scale, as those given in the two previous papers.

THOLEIITIC IGNEOUS ROCK SERIES

The following igneous rock series of tholeiitic type have been examined: two series from the Hakone volcano; two of the three series recognized among the Karroo dolerites; two of the three or more series to be found among the British Tertiary tholeiitic rocks; the Northfield sill; and the hybrid series of Satakunta. Data is also given for some of the more or less undifferentiated Hawaiian tholeiitic basalts. For comparison we have the results of trace element determinations for the Skaergaard intrusion (WAGER and MITCHELL, 1951), and for the sill near Dillsburg, Pennsylvania (HOTZ, 1953).

(a) *The Hakone series*

The lavas of the Hakone volcano and adjacent area have been described by KUNO (1950), and a wealth of chemical data has been provided by NAGASHIMA (1953). KUNO recognizes two series, a P (pigeonite) series and an H (hypersthene) series, characterized respectively by the occurrence of pigeonite and hypersthene in the groundmass. Many of the lavas are strongly porphyritic, representing accumulative rocks, and these are carefully distinguished by KUNO from those lavas which represent true liquids. Variation diagrams showing the relationships between Mg, $(Fe'' + Fe''')$ and $(Na + K)$, and between Ca, Na, and K for both series, are given in Figs. 31 and 32. The accumulative rocks have been omitted. The approximate composition of the supposed parental magma, common to both series, will be found in Table 32, col. 5.

(b) *The Karroo dolerites*

WALKER and POLDERVAART (1949) were able to recognize three trends amongst the Karroo dolerites: (i) the main trend, to which the majority of the rocks conform, characterized by a slight absolute enrichment in iron; (ii) an iron-rich trend, best

* Part I—*Geochim. et Cosmochim. Acta* (1953), **4**, 105; Part II—*ibid.* (1954) **5**, 245.

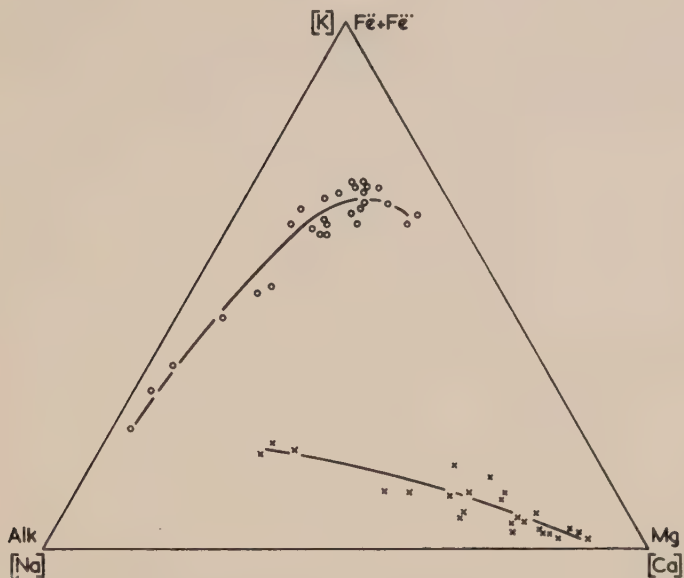


Fig. 31. Variation diagram of the Hakone P-series lavas (accumulative rocks omitted). Small circles refer to variation in $(Fe'' + Fe''')$, Mg, and $(Na + K)$; crosses refer to variation in Ca, Na, and K.

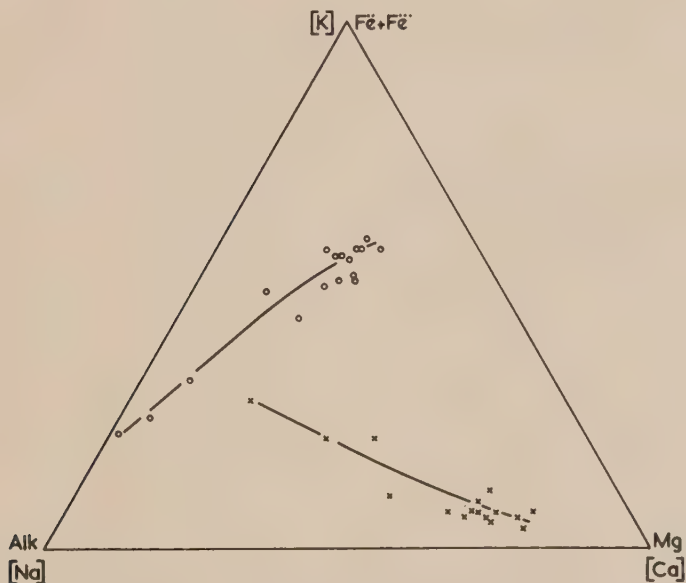


Fig. 32. Variation diagram of the Hakone H-series lavas (accumulative rocks omitted).

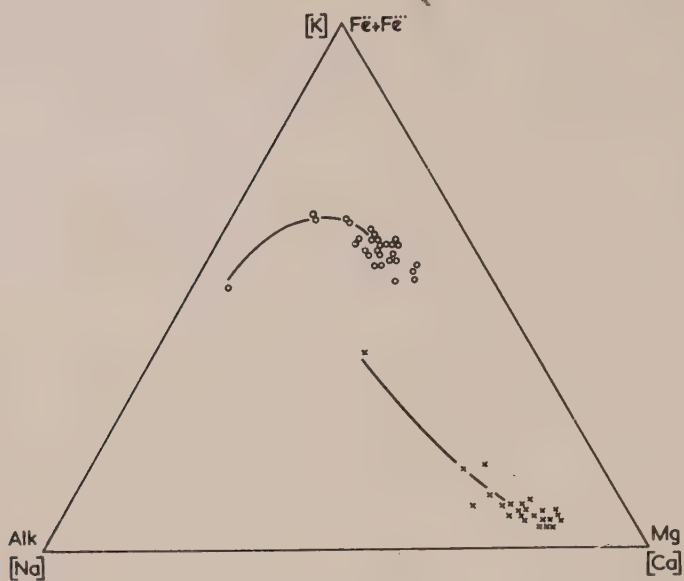


Fig. 33. Variation diagram of the main trend of the Karroo dolerites (accumulative rocks omitted).

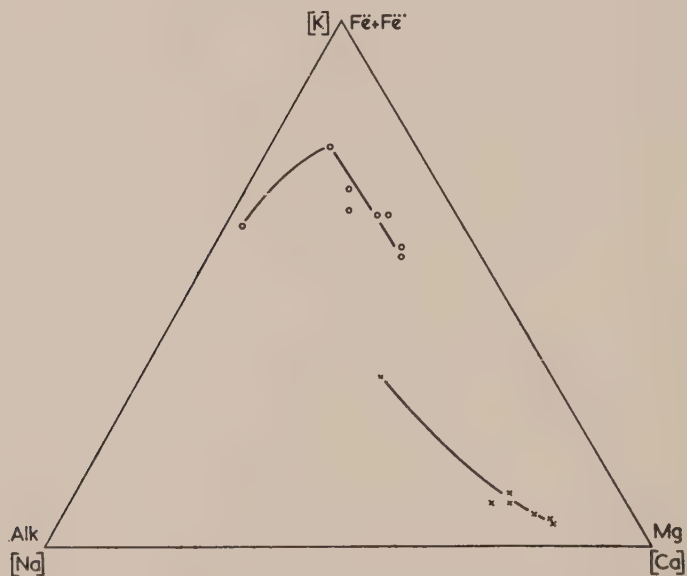


Fig. 34. Variation diagram of the iron-enriched trend of the Karroo dolerites (accumulative rocks omitted).

seen in the rocks of Elephant Head and New Amalfi, with considerable absolute enrichment in iron; (iii) a third trend in which there is no absolute enrichment in iron, and which is represented by relatively few analyses. Variation diagrams for the three trends, with accumulative rocks omitted, are given in Figs. 33, 34, and 35. The approximate composition of the supposed parental magma, common to the three series, will be found in Table 32, col. 2.

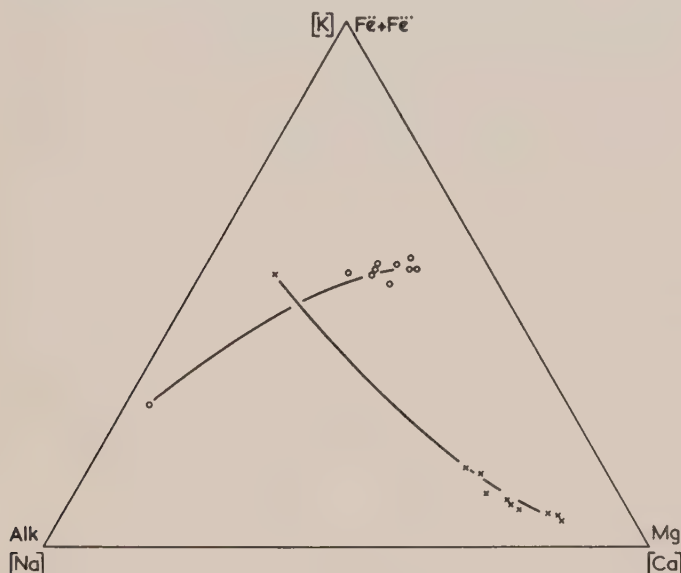


Fig. 35. Variation diagram of the third trend of the Karroo dolerites (accumulative rocks omitted).

(c) *British Tertiary tholeiitic rocks*

At least three trends may be recognized among the British Tertiary tholeiitic rocks, characterized, like those among the Karroo dolerites, by varying degrees of absolute enrichment in iron. There is a main trend with slight absolute enrichment in iron, a trend with no absolute enrichment in iron, and an iron-rich trend which is, however, better displayed among the rocks of Iceland and the Faroes. Variation diagrams for these three trends are given in Figs. 36, 37, and 38, again with accumulative rocks omitted. The approximate composition of the supposed parental magma, common to the three series, will be found in Table 32, col. 4.

The Tertiary tholeiitic igneous rocks of Greenland belong to the same petrographic province, and the rocks of the Skaergaard intrusion provide a fourth trend, with extreme absolute enrichment in iron (WAGER and DEER, 1939).

(d) *The Northfield Sill*

The differentiated Northfield Sill has been described by WALKER (1952). There is no absolute enrichment in iron at any stage. The variation diagram is given in Fig. 39, and the approximate composition of the supposed parental magma in Table 32, col. 6.

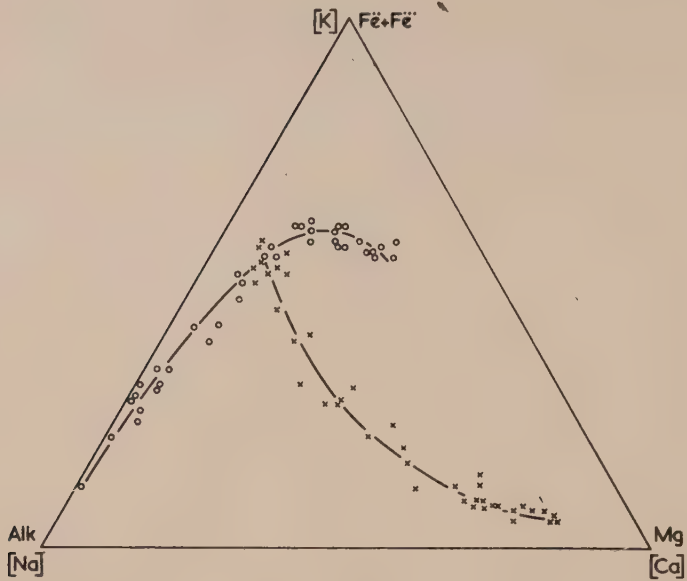


Fig. 36. Variation diagram of the main trend of British (and Icelandic) Tertiary tholeiitic rocks (accumulative rocks omitted).

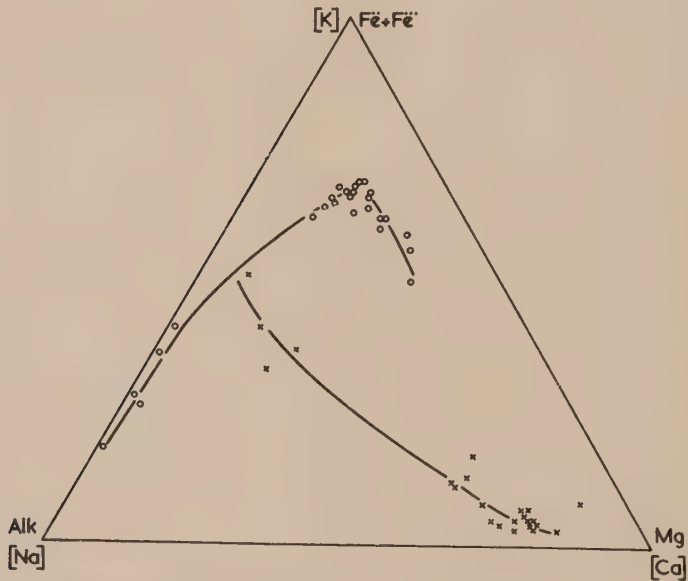


Fig. 37. Variation diagram of the iron-enriched trend of British (and Icelandic) Tertiary tholeiitic rocks (accumulative rocks omitted).

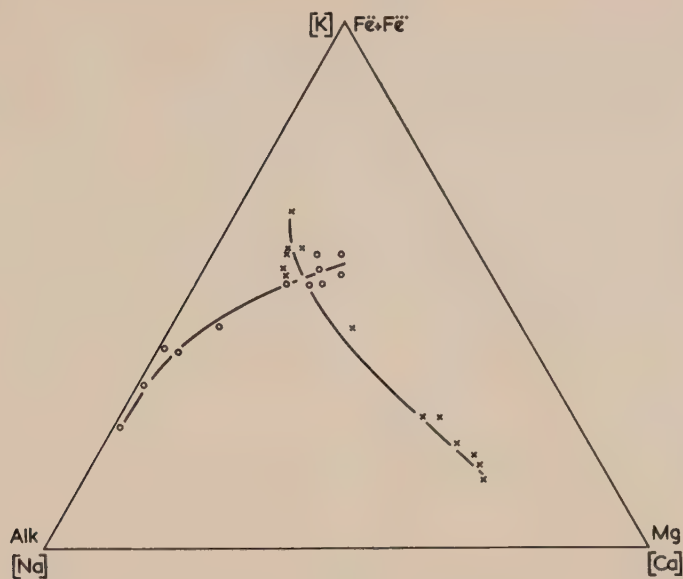


Fig. 38. Variation diagram of the third trend of British (and Icelandic) Tertiary tholeiitic rocks (accumulative rocks omitted).

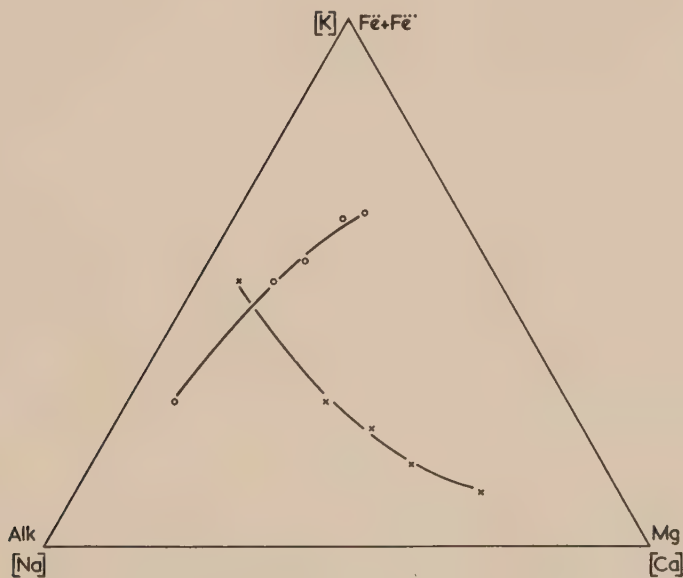


Fig. 39. Variation diagram of the rocks of the Northfield sill.



Figs. 40. Variation diagram of the rocks of the Dillsburg sill.

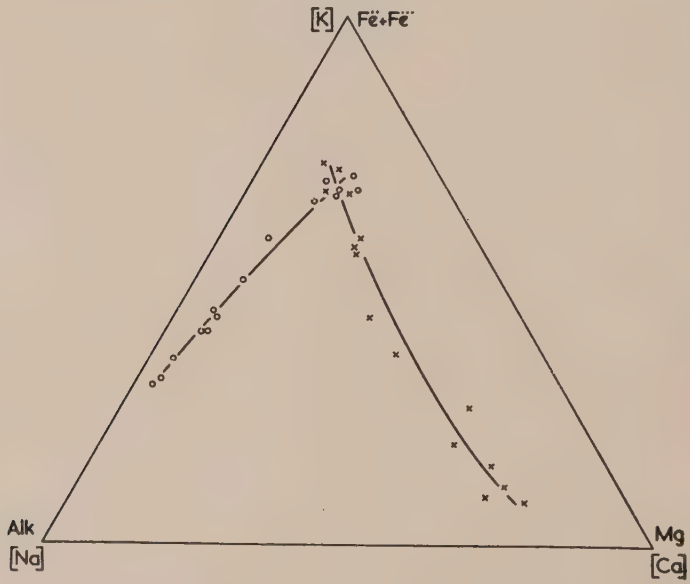


Fig. 41. Variation diagram of the Satakunta hybrids.

(e) *The differentiated sill near Dillsburg, Penn.*

The rocks from this sill have been described by HOTZ (1953), who has also provided some trace element data. Considerable absolute enrichment in iron occurs here during the differentiation process. The variation diagram is given in Fig. 40, and the composition of the parental magma in Table 32, col. 3.

(f) *Hawaiian tholeiitic basalts*

These have been described by WASHINGTON and, more recently, by MACDONALD (1949) [Hawaii] and by WENTWORTH and WINCHELL (1947) [Koolau Series, Oahu]. Their chemistry has been considered in particular detail by POWERS (1955). They show only slight differentiation, and the composition of the supposed parental magma is given in Table 32, col. 1.

(g) *The Satakunta hybrids*

This series of hybrids between an iron-rich dolerite and older rapakivi granite has been described in detail by KAHMA (1951). The variation diagram is given in Fig. 41.

VARIATION IN THE MAJOR AND TRACE ELEMENTS OF THE THOLEIITIC ROCK SERIES

The data on which the following discussion is based are given in Tables 18 to 31, so far as the trace elements are concerned. For the major elements we had, as in our previous papers, all the chemical data (recalculated on a water-free basis) available for each of the particular series. The diagrams illustrating the behaviour of the major, and some of the minor, elements along the supposed liquid line of descent in the various series, are given in Figs. 42 to 44. They were prepared in the same way as those of our previous papers.

(a) *Hakone lavas (Tables 18 and 19).*

Silicon and Oxygen (Figs. 42a, 42b). The behaviour of these two elements is not very different in the P- and H-series, but the curves for both elements are somewhat steeper in the latter series, and are virtually linear.

Aluminium and Gallium (Figs. 42a, 42b). Here again, the curves are very similar for both series, identical in fact in the case of gallium. But the Al curve runs at somewhat higher values in the intermediate stages for the H-series. In both series the Al and Ga curves run nearly parallel, though this is more perfectly the case in the P-series. The average ratio $\text{Ga} \times 1000/\text{Al}$ is 0.30 for the lavas of the P-series, and 0.26 for those of the H-series.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, Scandium, Titanium (Figs. 43a, 43b). Some of these elements behave differently in the two series, others behave in the same way. Thus the curves for Li and Co are identical in both series, the former element increasing in amount slowly but steadily as the value of the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, while the latter element decreases steadily in the same direction. On the other hand, the curves for Fe, Mg, Cr, Ni, and V are different. In the P-series there is slight absolute enrichment

in Fe towards the basic end, and this is accompanied by a marked maximum on the V curve. In the H-series there is no absolute enrichment in Fe, with the result that the Fe curve declines steadily. Similarly, there is no maximum on the V curve although this element remains almost constant for a time before decreasing in amount.

Figs. 42a-i. Variation in silicon, oxygen, aluminium, and gallium.
Values in weight per cent, with Ga $\times 1000$.

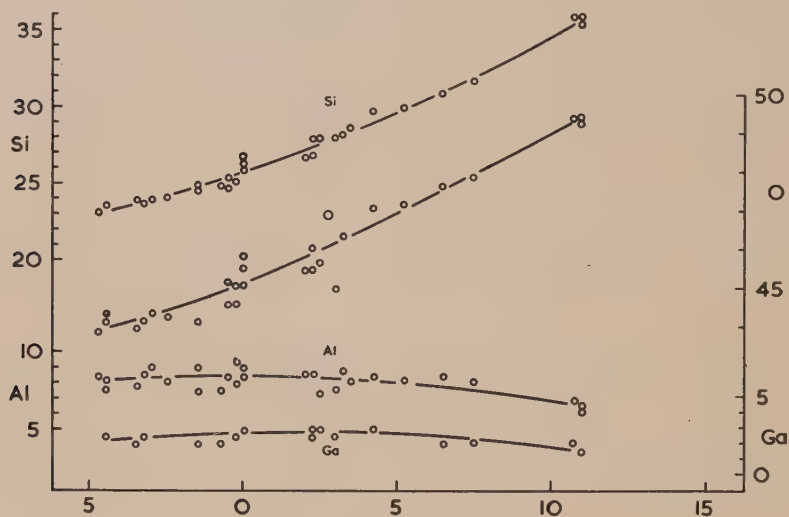


Fig. 42a. Hakone P-series.

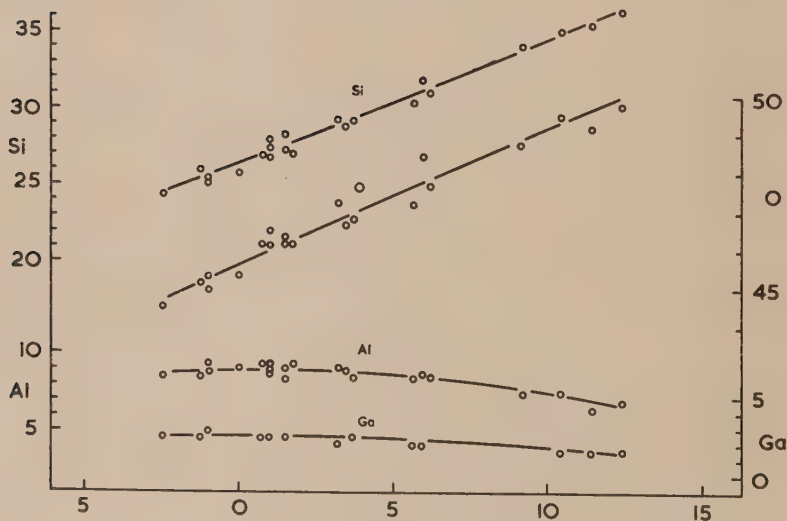


Fig. 42b. Hakone H-series.

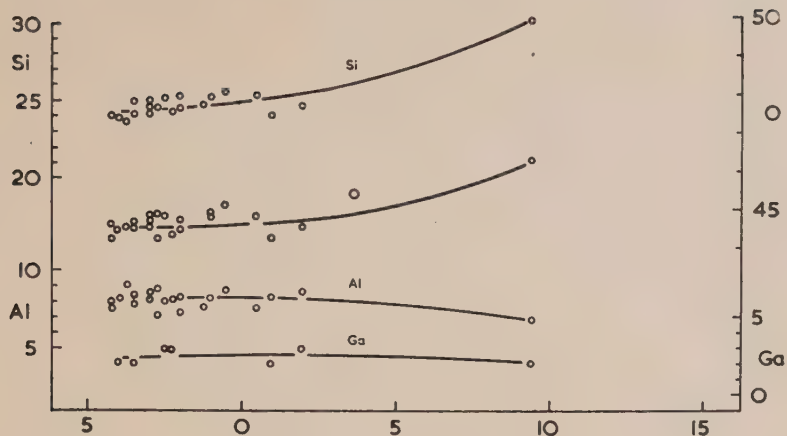


Fig. 42c. Karroo main trend.

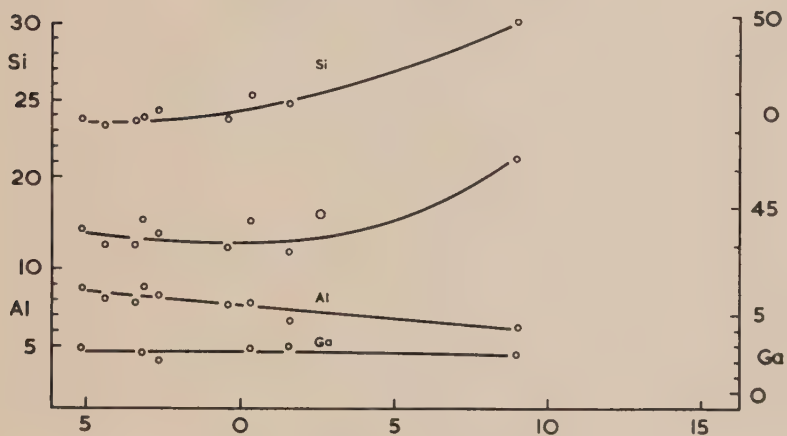


Fig. 42d. Karroo iron-enriched trend.

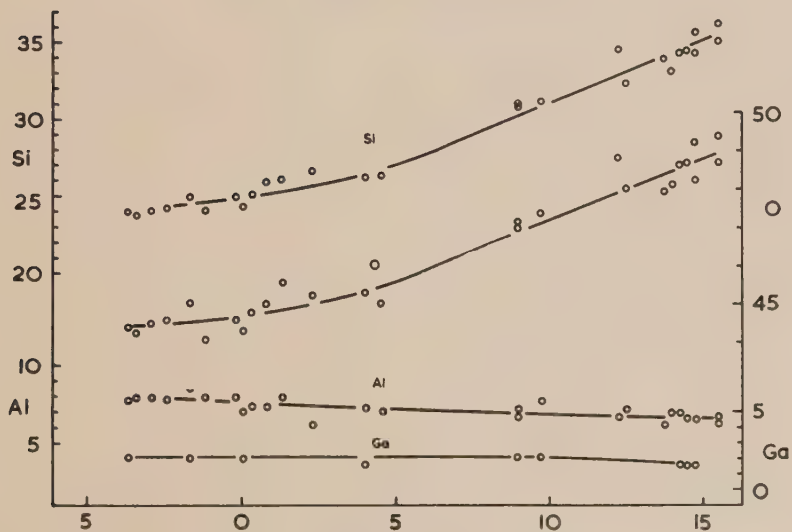


Fig. 42e. British Tertiary main trend.

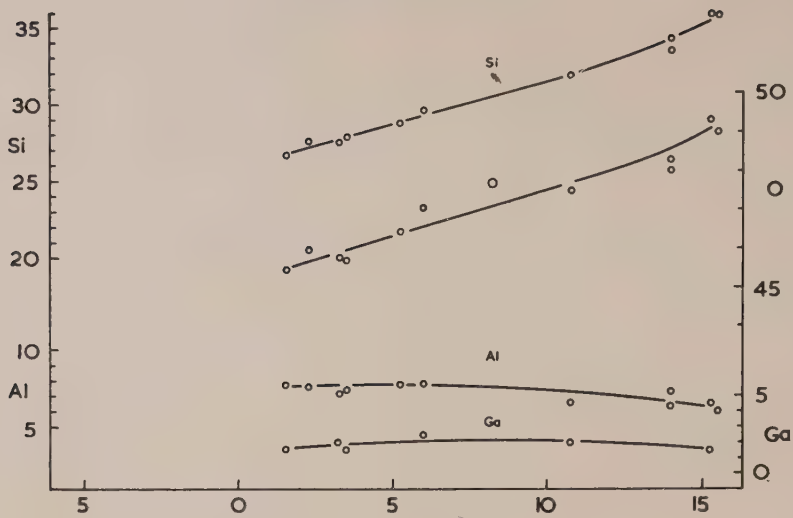


Fig. 42f. British Tertiary third trend.

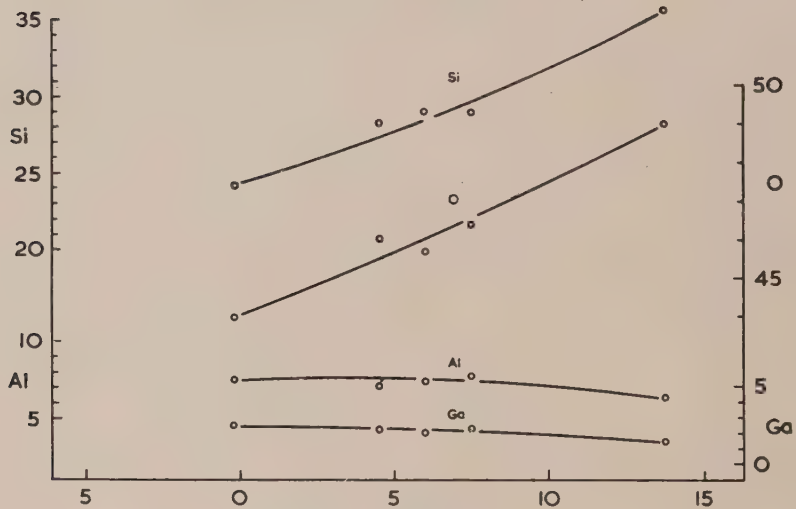


Fig. 42g. Northfield sill.

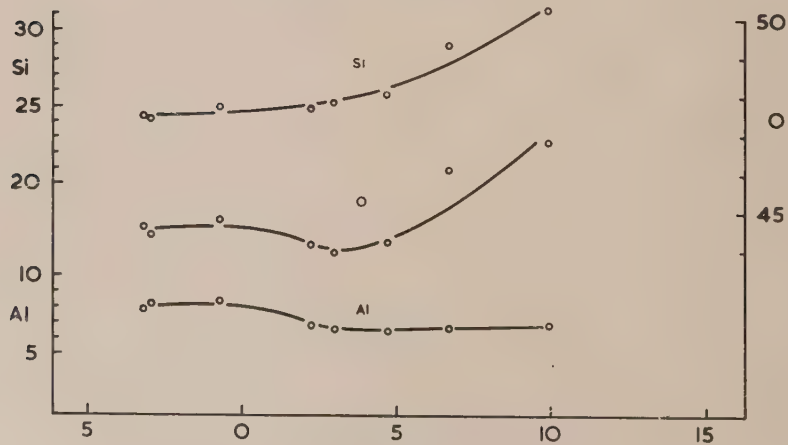


Fig. 42h. Dillsburg sill.

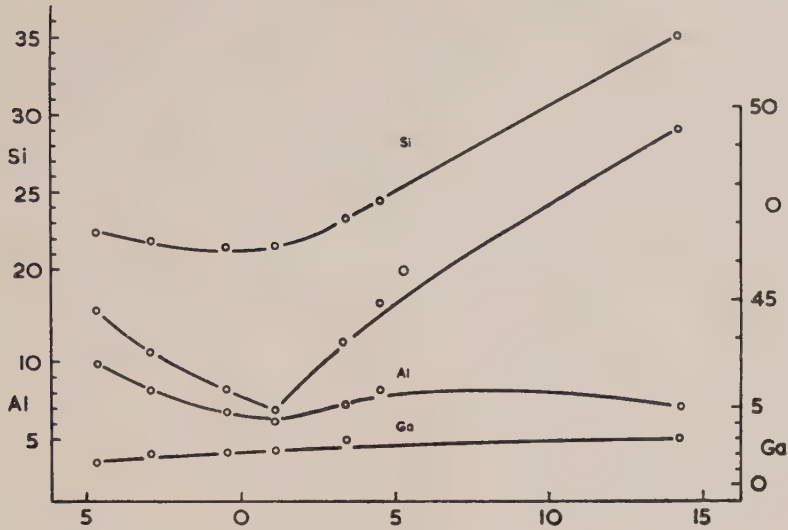


Fig. 42i. Skaergaard intrusion.

The main difference in the behaviour of Cr, Ni, and Mg is to be seen in the intermediate stages of the two series. In the P-series all three elements are being eliminated more rapidly than in the H-series, with the result that intermediate members of the latter are richer in these elements.

It will be noted that the parental magma of both series (represented by the points at the extreme basic end of the P-series curves) is relatively rich in Fe. In harmony with this it is relatively poor in Cr and Ni, rich in V, and has $\text{Co} > \text{Ni}$, so that the curve for Co lies above that for Ni in both series.

Scandium is present throughout in the rocks of the P-series, decreasing in amount as the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases in value. It is somewhat lower in amount in the H-series, and falls below the limit of sensitivity in the extreme acid member. Titanium is low in both series (but lower in the H-series than in the P-series), remains more or less constant for a time, but decreases in amount in the late-intermediate and late stages.

Calcium and Strontium (Figs. 44a, 44b). Calcium decreases steadily as the value of the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, and the curves for both series are very much alike. Strontium is low in both series, apparently passing through a feeble maximum in the P-series but declining more or less steadily in the H-series, where, however, the values run somewhat higher at the basic end.

Yttrium is present at all stages in both series and increases in amount as the value of the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ rises. The absolute values are slightly lower in the H-series, but the ratios $\text{Y} \times 1000/\text{Ca}$ are about the same in both.

Sodium (Figs. 44a, 44b) increases in amount in both series as the value of the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, but this increase is greater in the P-series than in the H-series.

Potassium, Barium, Rubidium, Lead (Figs. 44a, 44b). Potassium is low in both series, and the curves for this element are identical through much of their range.

Towards the acid end of the H-series, however, the K curve swings upwards, a feature lacking in the K curve of the P-series. Again, barium is relatively low throughout, but increases slowly (as does K), and once more the curves for both series are practically identical. The same remarks apply to the rubidium curves for the two series and, as is usual for most of the igneous rock series examined so far, the curves for Rb and K are more or less parallel. Lead appears in small amounts only in the extreme acid members of the P-series.

Zirconium is low in value at the basic end of both series and does not rise much beyond 100 p.p.m. in either.

Accumulative Rocks. Most of the accumulative rocks of the P-series (Table 18, cols. 1-8) are enriched to some extent in plagioclase feldspar, and these have lower Cr, Ni, Co, and Sc, with higher Sr and Ba, than corresponding normal rocks. Others are somewhat enriched in dark minerals as well (e.g., Table 18, cols. 1 and 3), and these have higher Cr and Ni than normal.

The accumulative rocks of the H-series which we have examined (Table 19, cols. 1-4) are somewhat enriched in dark minerals and are richer than usual in Cr, Ni, and, to a slight extent, in Co.

Three rocks (Table 18, cols. 27-29) fall off the normal P trend, having a higher degree of absolute enrichment in iron. In harmony with this, both Cr and Ni have fallen below their limits of sensitivity.

(b) *Karoo dolerites (Tables 20-23)*

We had adequate material for two of the trends recognized by WALKER and POLDERVAART, namely, the main trend and the iron-rich trend, but not for the third trend. Consequently, diagrams for the first two trends only are given here, though trace element determinations for a few samples belonging to the third trend will be found in Table 23. Unfortunately, the end-stage members of the other two trends have not yet been found and described or analysed, so neither of the sets of diagrams is complete.

Silicon and Oxygen (Figs. 42c, 42d). The curves for silicon and oxygen (as far as they go) are much flatter than those for the P- and H-series at Hakone, and the curves for these elements in the iron-rich trend are flatter in the earlier stages than those in the main trend.

Aluminium and Gallium (Figs. 42c, 42d). The Al and Ga curves for the Karoo main trend are virtually identical with those of the P-series at Hakone. In the iron-rich trend, however, Al declines steadily, while Ga remains constant. The average ratio, $\text{Ga} \times 1000/\text{Al}$, is 0.30 for the main trend and 0.35 for the iron-rich trend.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, Scandium, Titanium (Figs. 43c, 43d). The curves for Mg and Li are practically identical in both series, the former declining steadily, while the latter shows a gentle rise. The two curves for Co are also very similar, except that in the iron-rich trend the curve declines rather more steeply. In both trends Ni is in excess of Co in the early stages, but is eliminated more rapidly, so that the Co curves lie above the Ni curves in the later stages of each trend. Moreover, although Ni is higher in the earlier members of the iron-rich trend than in the corresponding members of the main

Figs. 43a-i. Variation in chromium, lithium, magnesium, nickel, cobalt, iron, and vanadium. Values in weight per cent with Cr, Li, Ni, Co, and V $\times 1000$.

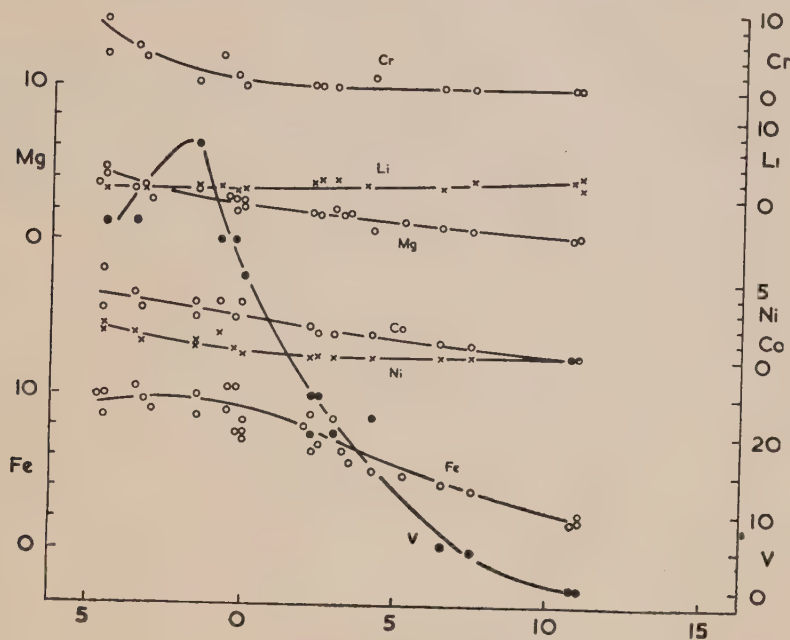


Fig. 43a. Hakone P-series.

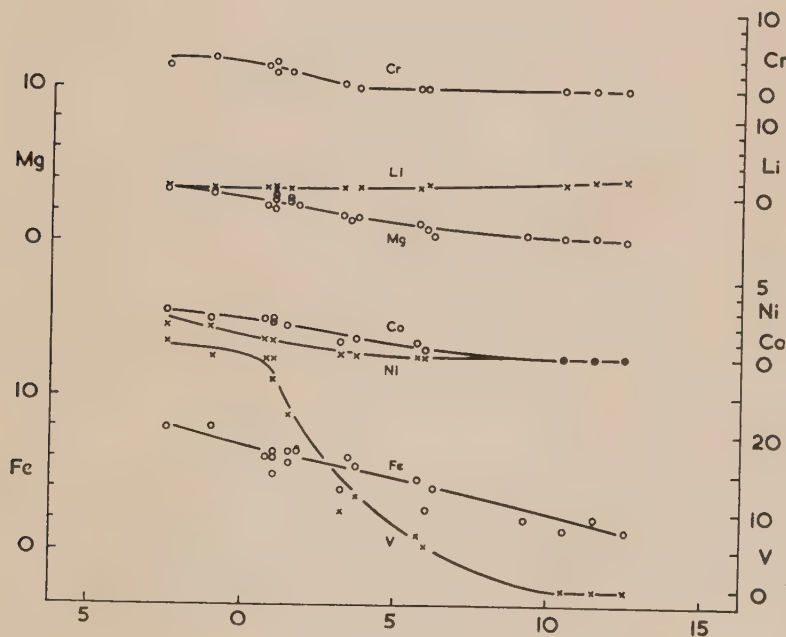


Fig. 43b. Hakone H-series.

Table 18. Lavas of Hakone and adjacent area. (1) P-series

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Si	226.10 ³	228.10 ³	216.10 ³	236.10 ³	238.10 ³	243.10 ³	245.10 ³	282.10 ³	237.10 ³	240.10 ³	238.10 ³	236.10 ³	245.10 ³	249.10 ³
Al	93.10 ³	106.10 ³	108.10 ³	104.10 ³	104.10 ³	105.10 ³	90.10 ³	91.10 ³	81.10 ³	77.10 ³	77.10 ³	85.10 ³	71.10 ³	75.10 ³
Ti	4.10 ³	1.10 ³	5.10 ³	5.10 ³	6.10 ³	5.10 ³	7.10 ³	4.10 ³	7.10 ³	2.10 ³	5.10 ³	7.10 ³	8.10 ³	5.10 ³
Fe ⁺⁺	27.10 ³	15.10 ³	21.10 ³	13.10 ³	16.10 ³	19.10 ³	20.10 ³	17.10 ³	8.10 ³	22.10 ³	27.10 ³	20.10 ³	32.10 ³	35.10 ³
Mg	49.10 ³	34.10 ³	41.10 ³	32.10 ³	22.10 ³	25.10 ³	33.10 ³	13.10 ³	41.10 ³	47.10 ³	33.10 ³	35.10 ³	29.10 ³	25.10 ³
Fe ⁺	61.10 ³	81.10 ³	60.10 ³	51.10 ³	66.10 ³	54.10 ³	67.10 ³	44.10 ³	78.10 ³	78.10 ³	78.10 ³	77.10 ³	78.10 ³	74.10 ³
Na	7.10 ³	9.10 ³	13.10 ³	10.10 ³	13.10 ³	14.10 ³	15.10 ³	24.10 ³	10.10 ³	8.10 ³	14.10 ³	11.10 ³	15.10 ³	17.10 ³
Ca	86.10 ³	96.10 ³	87.10 ³	94.10 ³	81.10 ³	78.10 ³	68.10 ³	51.10 ³	87.10 ³	80.10 ³	83.10 ³	81.10 ³	73.10 ³	70.10 ³
K	2.10 ³	2.10 ³	5.10 ³	2.10 ³	2.10 ³	2.10 ³	5.10 ³	5.10 ³	3.10 ³	2.10 ³	2.10 ³	4.10 ³	4.10 ³	5.10 ³
P	(220)	(tr.)	(435)	(395)	(395)	(565)	(960)	(435)	—	(tr.)	(565)	(220)	(1440)	(450)
Ga	20	20	20	25	25	30	30	25	25	25	20	25	20	20
Cr	175	30	120	25	25	45	5	*	85	40	50	35	20	40
V	285	400	270	450	450	500	450	175	350	600	550	400	575	450
Li	7	5	5	5	5	3	8	20	5	7	5	5	12	10
Ni	70	15	30	15	10	15	6	*	15	20	15	8	10	15
Co	40	35	30	30	30	35	25	15	30	55	40	30	35	35
Sc	30	50	50	50	35	45	35	30	55	60	50	50	45	60
Zr	50	40	40	40	70	50	50	75	40	45	40	40	45	70
Mn	(310)	(1470)	(1395)	(1550)	(1550)	(1240)	(775)	(1240)	(4340)	(1935)	(2170)	(1550)	(2400)	(1550)
Y	15	15	15	15	20	15	20	30	10	10	15	15	20	20
Sr	450	200	175	250	200	320	350	225	180	175	175	150	175	200
Pb	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Ba	85	70	90	100	125	125	150	200	90	70	70	80	175	150
Rb	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Fe	64	69	66	67	79	75	72	82	68	68	76	73	79	81
Mg	36	31	34	33	21	25	28	18	32	32	24	27	21	19
Fe	60	63	58	59	69	64	62	59	62	64	69	66	70	70
Mg	34	28	29	30	18	22	24	13	29	30	21	24	18	16
Alk	6	9	13	11	13	14	14	28	9	6	10	10	12	14
Position	-5.8	-5.2	-5.1	-4.5	-2.2	-2.0	-1.4	+3.5	-4.6	-4.5	-3.5	-3.3	-1.6	-0.1

Table 18a. Lavas of Hakone and adjacent area: P-series

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ga × 1000/Al	0.22	0.19	0.19	0.24	0.24	0.29	0.33	0.27	0.31	0.32	0.26	0.29	0.28	0.5
Cr × 1000/Mg	3.6	0.9	2.9	0.8	1.1	1.8	0.2	*	2.1	0.9	1.5	1.0	0.7	1.0
V × 1000/Mg	5.8	11.8	6.6	14.1	20.5	20.0	13.6	13.5	8.5	12.8	16.7	11.4	19.8	18.0
Li × 1000/Mg	0.1	0.1	0.1	0.2	0.2	0.1	0.2	1.5	0.1	0.1	0.2	0.1	0.4	0.4
Ni × 1000/Mg	1.4	0.4	0.7	0.5	0.5	0.6	0.2	*	0.4	0.4	0.5	0.2	0.3	0.6
Co × 1000/Mg	0.8	1.0	0.7	0.9	1.4	1.4	0.8	1.2	0.7	1.2	1.2	0.9	1.2	1.4
Fe/Mg	1.8	2.2	2.0	2.0	3.7	2.9	2.6	4.7	2.1	2.1	3.2	2.8	3.8	4.4
Cr × 1000/Fe	2.0	0.4	1.5	0.4	0.3	0.6	0.1	*	1.0	0.4	0.5	0.4	0.2	0.4
V × 1000/Fe	3.2	5.3	3.3	7.0	5.5	6.8	5.2	2.9	4.1	6.0	5.2	4.1	5.2	4.1
Co × 1000/Fe	0.5	0.5	0.4	0.5	0.4	0.5	0.3	0.2	0.3	0.5	0.4	0.3	0.3	0.5
Y × 1000/Ca	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.6	0.1	0.1	0.2	0.2	0.3	0.5
Sr × 100/Ca	0.5	0.2	0.2	0.3	0.2	0.4	0.5	0.4	0.2	0.2	0.2	0.2	0.2	0.3
Sr × 100/Ca + K	0.5	0.2	0.2	0.3	0.2	0.4	0.5	0.4	0.2	0.2	0.2	0.2	0.2	0.3
Ba × 100/K	4.2	3.5	1.8	5.0	6.2	6.2	3.0	4.0	3.0	3.5	3.5	2.0	4.4	3.0
Rb × 100/K	*	*	*	*	*	*	*	*	*	*	*	*	*	*

1. Olivine basalt [accumulative] (NAGASHIMA, anal. B, p. 15).
2. Hypersthene-olivine basalt [accumulative] (NAGASHIMA, anal. 66, p. 13).
3. Olivine-augite basalt [accumulative] (NAGASHIMA, anal. 21, p. 9).
4. Olivine basalt [accumulative] (NAGASHIMA, anal. 28, p. 10).
5. Augite-bearing olivine basalt [accumulative] (KUNO, anal. 5, p. 1000).
6. Hypersthene-augite-olivine basalt [accumulative] (KUNO, anal. 9, p. 1000).

7. Olivine-bearing hypersthene andesite [accumulative] (NAGASHIMA, anal. 39, p. 11).
8. Augite-hypersthene andesite [accumulative] (KUNO, anal. p. 1001).
9. Olivine basalt (aphyric band) (NAGASHIMA, anal. 34, p. 10).
10. Aphyric basalt (NAGASHIMA, anal. 67, p. 13).
11. Aphyric basalt (KUNO, anal. D, p. 1005).
12. Augite-bearing olivine basalt (NAGASHIMA, anal. 38, p. 11).
13. Hypersthene basalt (KUNO, anal. E, p. 1005).

Table 18. (contd.)

15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
249.10 ³ 78.10 ³ 8.10 ³ 31.10 ³ 26.10 ³ 75.10 ³ 17.10 ³ 64.10 ³ 4.10 ³	259.10 ³ 88.10 ³ 8.10 ³ 17.10 ³ 26.10 ³ 58.10 ³ 16.10 ³ 65.10 ³ 5.10 ³	278.10 ³ 85.10 ³ 7.10 ³ 10.10 ³ 18.10 ³ 53.10 ³ 15.10 ³ 61.10 ³ 9.10 ³	267.10 ³ 83.10 ³ 6.10 ³ 33.10 ³ 18.10 ³ 56.10 ³ 22.10 ³ 53.10 ³ 5.10 ³	278.10 ³ 72.10 ³ 6.10 ³ 31.10 ³ 17.10 ³ 63.10 ³ 24.10 ³ 63.10 ³ 11.10 ³	279.10 ³ 75.10 ³ 7.10 ³ 31.10 ³ 21.10 ³ 55.10 ³ 22.10 ³ 50.10 ³ 8.10 ³	296.10 ³ 84.10 ³ 7.10 ³ 13.10 ³ 8.10 ³ 38.10 ³ 15.10 ³ 56.10 ³ 8.10 ³	307.10 ³ 84.10 ³ 5.10 ³ 15.10 ³ 10.10 ³ 28.10 ³ 27.10 ³ 36.10 ³ 8.10 ³	315.10 ³ 80.10 ³ 4.10 ³ 8.10 ³ 7.10 ³ 30.10 ³ 35.10 ³ 32.10 ³ 8.10 ³	355.10 ³ 68.10 ³ 2.10 ³ 3.10 ³ 2.10 ³ 15.10 ³ 29.10 ³ 19.10 ³ 11.10 ³	350.10 ³ 64.10 ³ 2.10 ³ 21.10 ³ 3.10 ³ 4.10 ³ 33.10 ³ 16.10 ³ 11.10 ³	357.10 ³ 61.10 ³ 3.10 ³ 10.10 ³ 3.10 ³ 4.10 ³ 31.10 ³ 17.10 ³ 12.10 ³	239.10 ³ 65.10 ³ 4.10 ³ 36.10 ³ 29.10 ³ 100.10 ³ 14.10 ³ 75.10 ³ 4.10 ³	285.10 ³ 69.10 ³ 4.10 ³ 20.10 ³ 13.10 ³ 68.10 ³ 20.10 ³ 50.10 ³ 13.10 ³	291.10 ³ 80.10 ³ 6.10 ³ 24.10 ³ 7.10 ³ 51.10 ³ 17.10 ³ 47.10 ³ 8.10 ³
(350) 25 15 450 6 6 25 35 50 (1705) 20 200 125 80 20	— 30 * 400 8 * 35 45 70 (1550) 45 225 * 80 *	(1135) 25 * 200 15 * 20 100 (1395) 30 250 * 180 75	(350) 30 * 250 15 * 80 100 (1705) 30 250 * 180 *	(435) 30 * 250 20 * 100 125 (850) 35 300 * 300 75	(220) 25 * 200 18 * 15 30 (1395) 35 300 * 300 75	(2840) 30 12 225 12 * 80 100 (1160) 30 370 * 300 *	(1570) 20 12 55 10 * 100 35 325 * 300 *	(785) 20 20 50 20 * 125 30 320 * 350 *	(655) 20 * * 20 * 10 150 10 475 75	(1395) 15 * * 10 * 35 175 10 475 35	(830) 15 * * 25 * 125 35 200 10 475 35	(tr.) 20 * 600 15 * 30 60 (1085) 20 125 * 150 *	(85) 25 * 220 10 * 30 125 (1160) 35 500 * 350 75	(1225) 25 * 125 8 * 15 30 80 (1935) 35 300 * 300 10
80 20 69 17 14	74 26 62 21 17	78 22 60 17 23	83 17 67 13 20	80 20 61 14 25	80 20 63 15 22	86 14 62 10 28	81 19 49 11 40	84 16 43 8 49	90 10 30 3 67	89 11 35 4 61	87 13 23 3 74	82 18 74 16 10	87 13 65 10 25	91 9 70 7 23
-0.3	±0.0	+2.3	+2.3	+2.4	+3.0	+4.3	+6.4	+7.4	+10.8	+10.9	+11.1	-2.0	+4.5	+5.1

Table 18a. (contd.)

15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
0.32	0.34	0.29	0.36	0.42	0.33	0.36	0.24	0.25	0.29	0.23	0.25	0.31	0.36	0.31
0.6 17.3 0.2 0.2 1.0 4.1	* 15.4 0.3 * 1.3 2.9	* 11.1 0.8 * 1.1 3.5	* 13.9 0.8 * 1.4 4.9	* 14.7 1.2 * 0.9 4.1	* 9.5 0.9 * 0.7 4.1	1.5 28.1 1.5 * 1.9 6.4	* 5.5 1.0 * 1.0 4.3	* 7.1 2.9 * 1.1 5.4	* * 10.0 * * 9.0	* * 3.3 * * 8.3	* * 8.3 * * 6.7	* 20.7 0.5 * 1.0 4.7	* 16.9 0.8 * 1.5 6.8	* 17.9 1.1 * 2.1 10.7
0.1 4.2 0.2	* 5.3 0.5	* 3.2 0.3	* 2.8 0.3	* 3.6 0.2	* 2.3 0.2	0.2 4.4 0.3	* 1.3 0.2	* 1.3 0.2	* * *	* * *	* * *	* 4.4 0.2	* 2.5 0.2	* 1.7 0.2
0.3 0.3 0.3	0.7 0.3 0.3	0.5 0.4 0.4	0.6 0.5 0.4	0.6 0.5 0.4	0.7 0.6 0.5	0.5 0.7 0.6	1.0 0.9 0.7	0.9 1.0 0.8	1.8 0.8 0.5	2.2 1.1 0.6	2.1 1.2 0.7	0.3 0.2 0.2	0.7 1.0 0.8	0.7 0.6 0.5
3.1 *	1.6 *	2.8 *	3.6 *	3.0 *	3.7 *	3.7 *	3.7 *	4.4 *	4.3 *	4.3 *	4.0 0.3	3.7 *	2.7 *	3.8 0.1

4. Hypersthene-augite-olivine basalt (NAGASHIMA, anal. 58, p. 12).
 5. Aphyric basalt (KUNO, anal. 20, p. 1004).
 6. Aphyric andesite (NAGASHIMA, anal. 23, p. 10).
 7. Aphyric andesite (NAGASHIMA, anal. 41, p. 11).
 8. Aphyric andesite (KUNO, anal. 21, p. 1004).
 9. Glassy aphyric andesite (NAGASHIMA, anal. 40, p. 11).
 10. Aphyric andesite (NAGASHIMA, anal. 53, p. 12).
 11. Hypersthene-augite andesite (NAGASHIMA, anal. 26, p. 10).
 12. Almost aphyric hypersthene-augite andesite (NAGASHIMA, anal. 7, p. 9).

23. Augite-hypersthene andesite (KUNO, anal. 23, p. 1004).
 24. Augite-bearing hypersthene dacite-obsidian (NAGASHIMA, anal. 20, p. 9).
 25. Aphyric dacite (NAGASHIMA, anal. 35, p. 11).
 26. Augite-bearing hypersthene dacite (NAGASHIMA, anal. 8, p. 9).
 27. Aphyric basalt (NAGASHIMA, anal. 69, p. 13).
 28. Aphyric andesite (NAGASHIMA, anal. 56, p. 12).
 29. Aphyric andesite (NAGASHIMA, anal. 27, p. 10).

Table 19. Lavas of Hakone and adjacent area. (2) H-series

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Si	243.10 ³	256.10 ³	264.10 ³	272.10 ³	243.10 ³	259.10 ³	250.10 ³	268.10 ³	267.10 ³	274.10 ³	272.10 ³	291.10 ³	291.10 ³	302.10 ³	317.10 ³	348.10 ³	352.10 ³	361.10 ³
Al	85.10 ³	91.10 ³	75.10 ³	90.10 ³	86.10 ³	85.10 ³	88.10 ³	93.10 ³	94.10 ³	86.10 ³	84.10 ³	91.10 ³	91.10 ³	83.10 ³	86.10 ³	79.10 ³	83.10 ³	89.10 ³
Ti	7.10 ³	7.10 ³	3.10 ³	5.10 ³	1.10 ³	16.10 ³	27.10 ³	18.10 ³	24.10 ³	20.10 ³	31.10 ³	15.10 ³	15.10 ³	15.10 ³	12.10 ³	2.10 ³	2.10 ³	1.10 ³
Fe ⁺⁺⁺	52.10 ³	32.10 ³	28.10 ³	26.10 ³	27.10 ³	28.10 ³	32.10 ³	23.10 ³	24.10 ³	30.10 ³	31.10 ³	35.10 ³	35.10 ³	32.10 ³	30.10 ³	2.10 ³	4.10 ³	5.10 ³
Mg	64.10 ³	50.10 ³	54.10 ³	41.10 ³	57.10 ³	52.10 ³	53.10 ³	42.10 ³	39.10 ³	40.10 ³	33.10 ³	37.10 ³	40.10 ³	32.10 ³	14.10 ³	9.10 ³	13.10 ³	2.10 ³
Fe ^v	17.10 ³	22.10 ³	19.10 ³	24.10 ³	19.10 ³	18.10 ³	21.10 ³	21.10 ³	20.10 ³	21.10 ³	21.10 ³	24.10 ³	24.10 ³	28.10 ³	27.10 ³	26.10 ³	24.10 ³	30.10 ³
Na	58.10 ³	62.10 ³	64.10 ³	56.10 ³	79.10 ³	74.10 ³	67.10 ³	63.10 ³	57.10 ³	57.10 ³	57.10 ³	58.10 ³	58.10 ³	48.10 ³	41.10 ³	22.10 ³	19.10 ³	11.10 ³
K	5.10 ³	8.10 ³	7.10 ³	5.10 ³	7.10 ³	4.10 ³	7.10 ³	4.10 ³	5.10 ³	6.10 ³	9.10 ³	6.10 ³	6.10 ³	8.10 ³	4.10 ³	13.10 ³	21.10 ³	16.10 ³
P	(700)	(85)	(525)	(565)	(1310)	(565)	(130)	(350)	(480)	(700)	(700)	(565)	(260)	—	(1180)	(1265)	(1295)	(11)
Ga	20	30	25	25	25	25	30	25	25	25	25	25	25	20	20	15	15	15
Cr	275	175	8	100	30	250	40	30	20	35	225	100	120	70	55	*	*	*
V	300	250	250	250	320	300	300	300	270	300	300	100	10	10	15	15	20	20
Li	8	10	10	8	10	10	10	12	10	8	20	10	10	8	*	*	*	*
Na	110	70	10	50	50	95	20	10	22	95	20	10	15	10	5	10	*	*
Co	35	35	25	30	30	35	30	25	20	30	15	15	15	20	15	10	*	*
Sc	30	15	30	70	30	80	70	70	80	85	80	45	70	70	70	120	120	120
Zr	65	85	70	70	80	65	70	70	80	85	80	15	15	20	15	10	120	120
Mn	(1550)	(1010)	(1395)	(1160)	(1395)	(1705)	(1240)	(1080)	(1240)	(1470)	(1395)	(1550)	(1395)	(2400)	(980)	(1315)	(850)	(385)
Y	15	15	25	25	15	15	15	15	15	30	60	275	325	250	275	225	175	125
Sr	350	500	300	350	350	225	500	250	300	300	300	275	325	250	275	225	175	125
Pb	*	200	200	150	100	150	175	175	170	225	275	200	150	300	225	475	500	600
Ba	*	200	200	150	100	150	175	175	170	225	275	200	150	300	225	475	500	600
Rb	*	200	200	150	100	150	175	175	170	225	275	200	150	300	225	475	500	600
Fe	60	68	76	68	71	71	71	72	70	67	70	70	76	80	74	82	84	96
Mg	40	32	24	32	29	29	29	28	30	33	30	30	24	20	26	18	16	4
Fe	52	52	62	51	59	57	57	56	55	51	54	44	57	49	39	25	30	22
Mg	34	25	20	23	24	24	23	21	23	26	23	20	18	12	14	5	6	1
Alk	14	23	18	26	17	19	20	23	22	23	23	36	25	39	47	70	64	77
Position	-2.4	-0.1	+0.3	+1.4	-2.5	-1.2	-0.9	+0.7	+1.0	+1.0	+1.5	+3.3	+3.7	+5.7	+6.0	+10.4	+11.5	+12.4

Table 19a. Lavas of Hakone and adjacent area: H-series

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Ga × 1000/Al	0.24	0.33	0.33	0.28	0.29	0.29	0.34	0.27	0.27	0.29	0.30	0.22	0.30	0.24	0.23	0.20	0.24	0.22
Cr × 1000/Mg	5.3	5.5	0.3	3.8	0.9	0.9	1.2	1.3	0.7	1.2	0.7	0.4	*	*	*	*	*	*
V × 1000/Mg	5.8	7.8	9.0	9.6	0.4	9.0	13.0	0.5	10.0	10.0	8.0	5.9	7.2	5.8	6.1	*	*	*
Li × 1000/Mg	0.2	0.3	0.4	0.3	0.3	0.4	0.6	0.4	0.4	0.3	0.4	0.6	0.5	0.8	1.7	5.0	5.0	40.0
Na × 1000/Mg	2.1	2.2	0.3	1.9	0.6	0.3	0.6	0.4	0.4	0.3	0.7	*	0.5	*	*	*	*	*
Co × 1000/Mg	0.7	1.1	0.9	1.1	0.9	0.9	0.8	1.1	0.8	0.8	0.7	0.6	0.9	0.8	0.6	4.7	5.2	26.0
Fe/Mg	1.5	2.1	3.1	2.2	2.5	2.4	2.5	2.6	2.3	2.0	2.3	2.3	3.2	3.9	2.9	4.7	5.2	26.0
Cr × 1000/Fe	3.5	2.6	0.1	1.8	0.4	*	0.5	0.5	0.3	0.6	0.3	0.2	*	*	*	*	*	*
V × 1000/Fe	3.8	3.7	2.8	4.5	3.8	3.7	3.7	5.0	4.3	5.0	3.4	2.6	2.2	1.5	2.1	*	*	*
Co × 1000/Fe	0.4	0.5	0.3	0.5	0.4	0.4	0.3	0.4	0.3	0.4	0.3	0.3	0.3	0.2	0.2	*	*	*
Y × 1000/Ca	0.3	0.2	0.4	0.4	0.2	0.3	0.2	0.2	0.3	0.5	0.3	0.3	0.4	0.6	0.6	1.4	1.6	2.3
Sr × 100/Ca	0.6	0.8	0.5	0.6	0.4	0.3	0.7	0.4	0.5	0.5	1.1	0.5	0.6	0.6	0.7	1.0	0.9	1.1
Str × 100/Ca + K	0.6	0.7	0.4	0.6	0.4	0.3	0.7	0.4	0.5	0.5	0.9	0.5	0.6	0.5	0.6	0.6	0.4	0.5
Ba × 100/K	1.4	2.5	2.9	3.0	1.4	3.8	2.5	4.4	3.4	3.7	3.1	3.3	1.9	3.7	5.6	3.7	2.4	3.8
Rb × 100/K	*	*	*	*	*	*	*	*	*	*	0.1	*	*	*	*	0.3	0.2	0.3

- Olivine basalt faccumulative (NAGASHIMA, anal. 51, p. 12).
- Aphyric olivine andesite faccumulative (NAGASHIMA, anal. 37, p. 11).
- Augite-hypersthene andesite faccumulative (NAGASHIMA, anal. 70, p. 13).
- Olivine-augite-hypersthene andesite faccumulative (NAGASHIMA, anal. A, p. 14).
- Almost aphyric olivine basalt (NAGASHIMA, anal. 13, p. 9).
- Aphyric hypersthene-augite-hypersthene andesite (NAGASHIMA, anal. 24, p. 10).
- Augite-olivine basalt (NAGASHIMA, anal. 50, p. 12).
- Olivine-bearing hypersthene-augite andesite (KINO, anal. 14, p. 1000).
- Augite-hypersthene andesite (NAGASHIMA, anal. 83, p. 14).
- Olivine basalt with xenocrysts of quartz and plagioclase (NAGASHIMA, anal. 85, p. 14).
- Hypersthene-hornblende-quartz dacite (NAGASHIMA, anal. 22, p. 9).
- Almost aphyric augite-hypersthene andesite (NAGASHIMA, anal. 43, p. 11).
- Augite-hypersthene andesite (NAGASHIMA, anal. 32, p. 10).
- Green hornblende-augite-hypersthene dacite (NAGASHIMA, anal. 29, p. 10).
- Augite-bearing hypersthene dacite (NAGASHIMA, anal. 29, p. 10).
- Augite-bearing hypersthene dacite-obsidian (NAGASHIMA, anal. 5, p. 9).

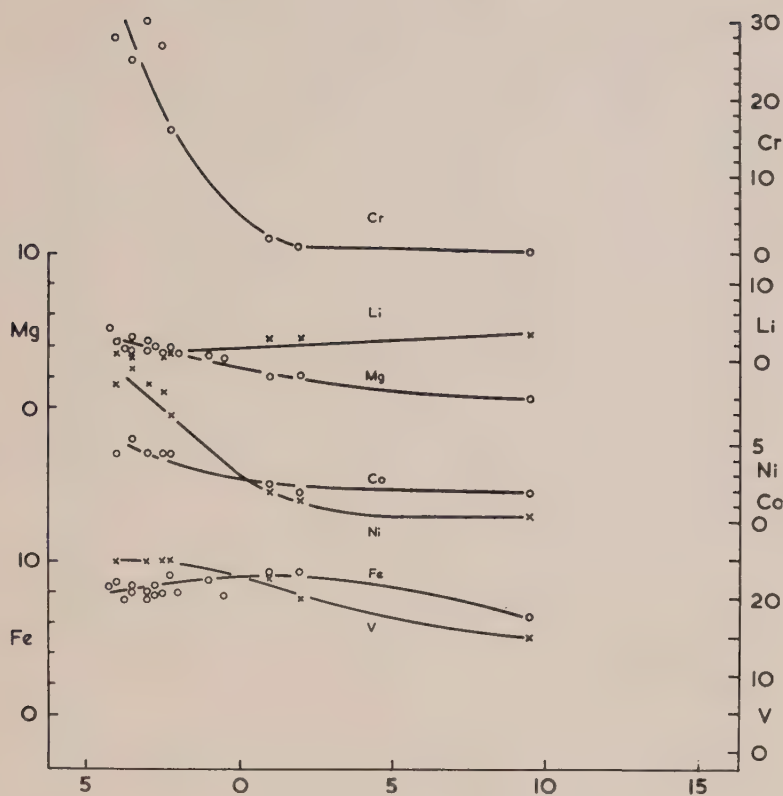


Fig. 43c. Karroo main trend.

trend, it falls below the limit of sensitivity earlier in the former. The same applies to chromium.

Iron shows slight absolute enrichment in the early intermediate stage of the main trend, and this feature is shown more markedly, of course, in the iron-rich trend. The vanadium curve shows no maximum in the first case, though there is possibly a feeble maximum on the V curve, earlier than the Fe maximum, in the second case. Vanadium is, however, being eliminated much more rapidly in the iron-rich trend than in the main trend.

Scandium appears in appreciable amounts in most of the rocks examined from all three trends, but falls below the limit of sensitivity at a quite early stage in the iron-rich trend, just about the time when Fe reaches its maximum. Titanium is relatively low in the early stages of all three trends. It reaches a maximum at about the same time as Fe in both the main and iron-rich trends.

Calcium and Strontium (Figs. 44c, 44d). The curves for calcium are almost identical in both trends. Strontium is low in both but tends to be higher in the main trend than in the iron-rich trend.

Yttrium is present in all the rocks examined. It shows some increase in the later members of the main trend, but this is more pronounced in the later members of the iron-rich trend.

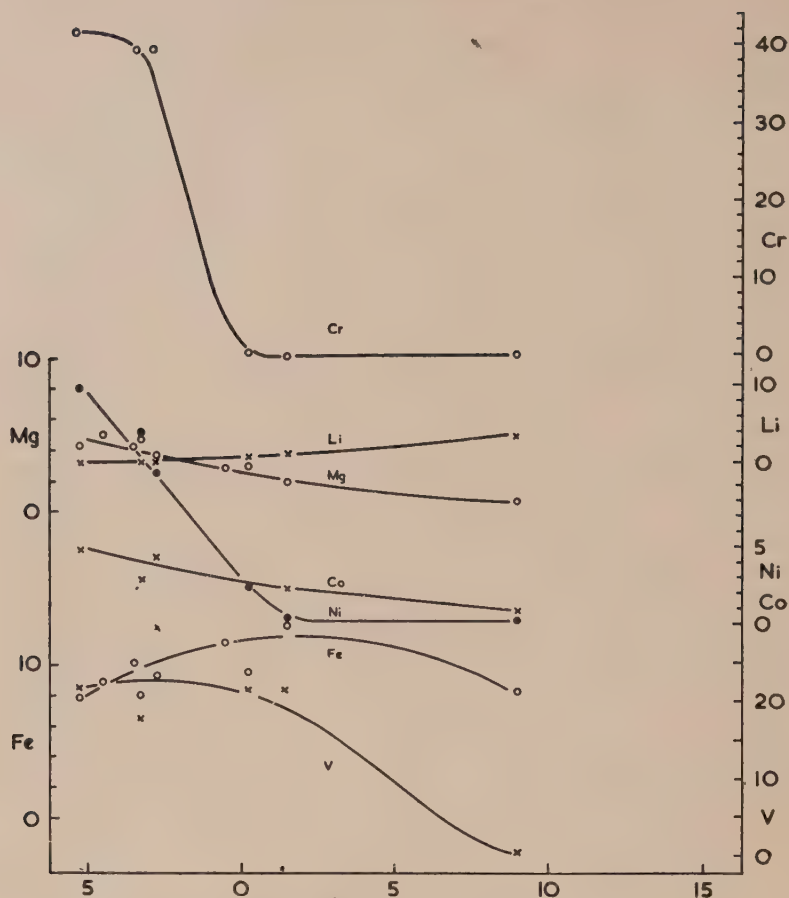


Fig. 43d. Karroo iron-enriched trend.

Sodium (Figs. 44c, 44d). The curves for sodium are identical in the two trends, the amount of Na increasing slightly as the value of the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ rises. The form of the curves is very close to that of the H-series at Hakone.

Potassium, Barium, Rubidium, Lead (Figs. 44c, 44d). The curves for K and Rb rise rather more sharply in the main trend than in the iron-rich trend as the function $[(\frac{1}{3} \text{ Si} + \text{K}) + (\text{Ca} + \text{Mg})]$ increases in value. The curves for Ba, however, are very similar in both trends, though Ba tends to be higher in the early members of the main trend than in those of the iron-rich trend. Once more the curves for Rb and K run more or less parallel in both trends. Lead is below the limit of sensitivity in all the rocks examined.

Compared with the P- and H-series of Hakone, the intermediate members of both Karroo trends are richer in K, Ba, and Rb.

Zirconium is higher in the basic members of the trends here than in those of the P- and H-series at Hakone. The amount tends to increase as the value of the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ rises, and this is especially marked in the late

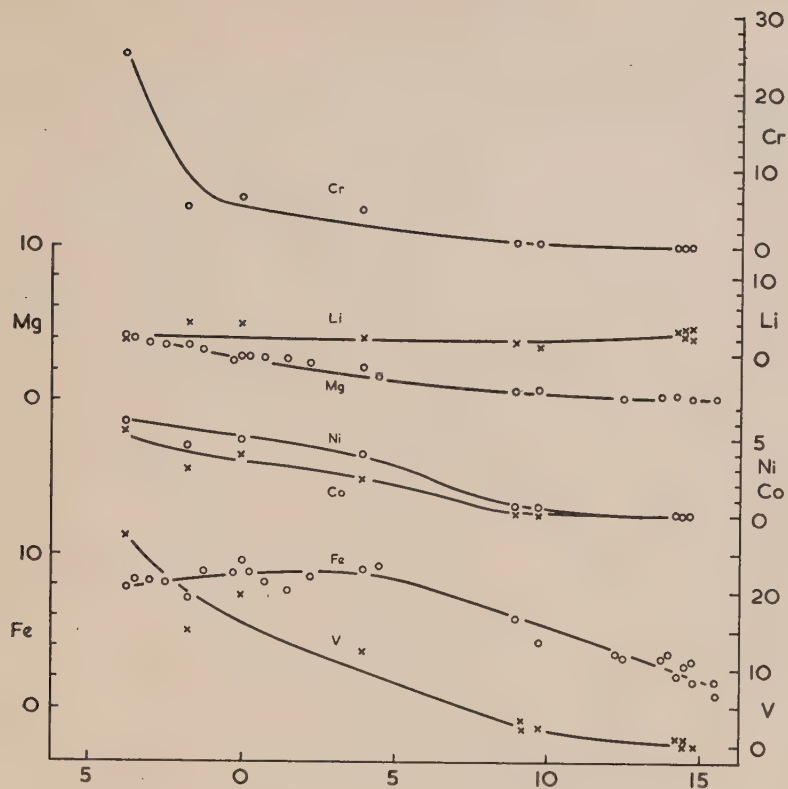


Fig. 43e. British Tertiary main trend.

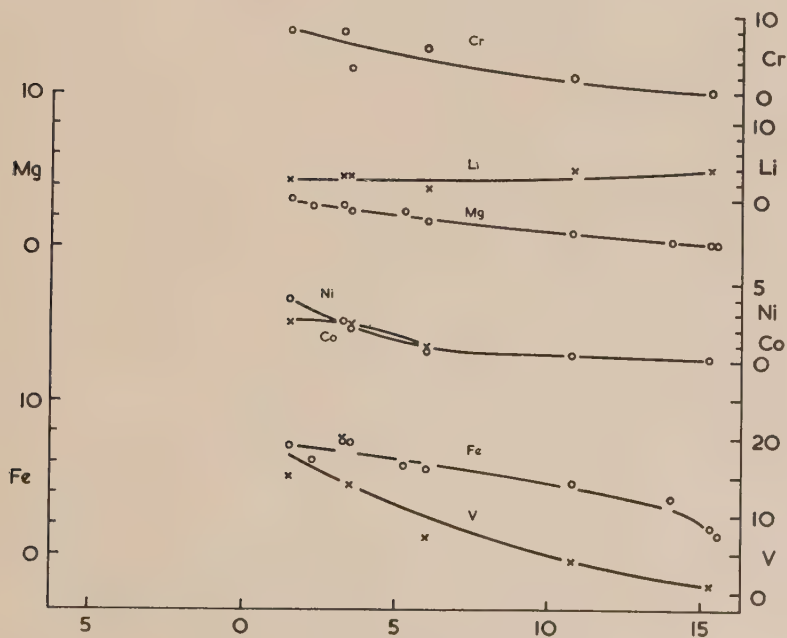


Fig. 43f. British Tertiary third trend.

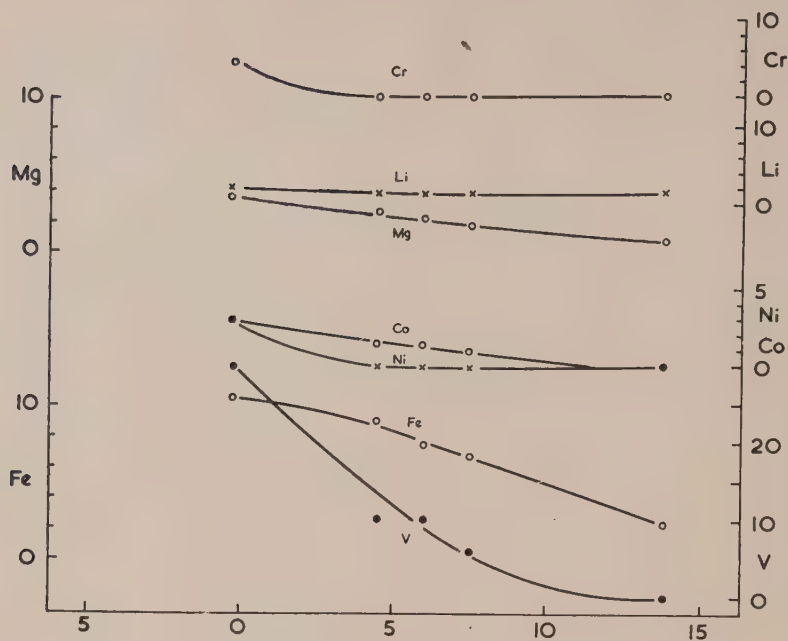


Fig. 43g. Northfield sill.

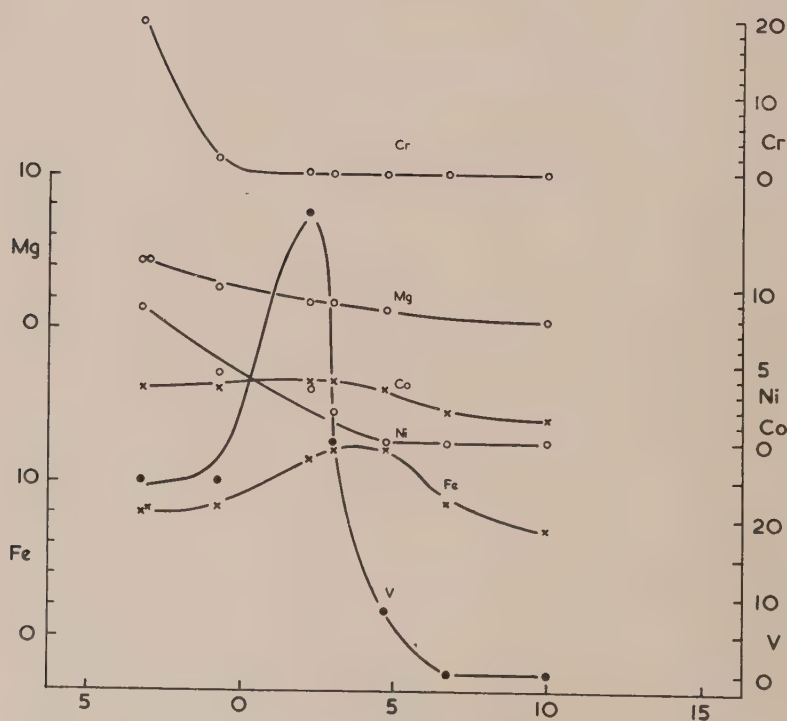


Fig. 43h. Dillsburg sill.

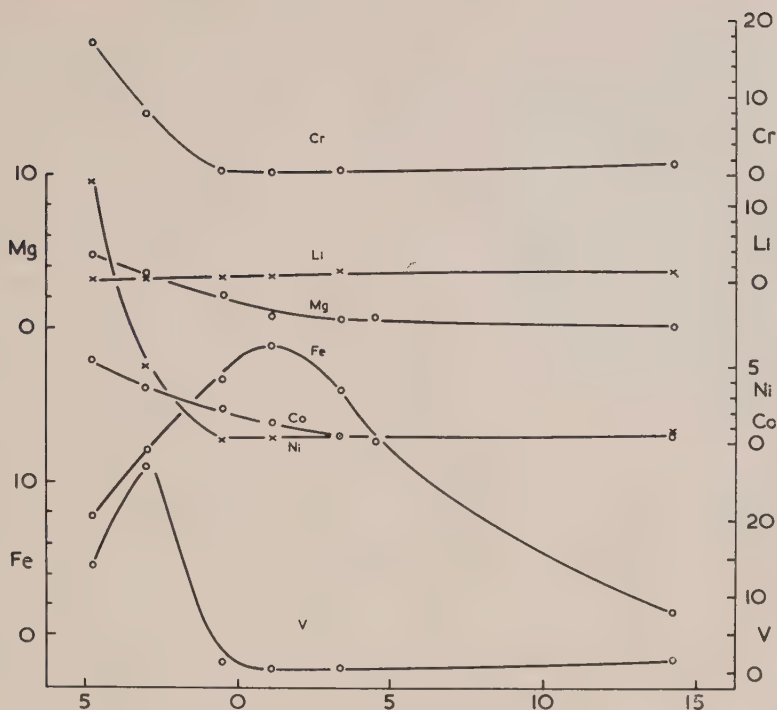


Fig. 43i. Skaergaard intrusion.

member of the iron-rich trend. This rock (Table 22, col. 9) is also the only one in which lanthanum and molybdenum have been detected.

The parental magma of the Karroo dolerite trends is believed to be represented by the extreme basic end-member of the iron-rich trend. If the curves for both the major and minor elements are extrapolated at the basic end of the main trend, they will be found to pass almost exactly through the points representing the basic end-member of the iron-rich trend.

Some data for the Mount Arthur tholeiites are given separately in Table 21. These rocks fall fairly well on the main trend, but are poorer in Ni and sometimes in Cr and Co. It is possible that this anomaly is due to alteration as "alteration is pronounced in all the rocks" (WALKER and POLDERVAART, 1949, p. 621).

Accumulative Rocks. The accumulative rocks belonging to the main trend which we have examined (Table 20, cols. 1-4), are all enriched to a varying degree in dark minerals, the first being rich in olivine. As a result, Cr, Ni, and Co are higher than usual, while Ga, V, Sc, Zr, Y, Sr, and Ba are, in general, lower.

The accumulative rocks belonging to the iron-rich trend are also enriched in dark minerals (Table 22, cols. 1-3), and the first two rocks are similar in their behaviour to, but more extreme than, the accumulative rocks of the main trend. The third rock represents a relatively late-stage accumulative type, enriched largely in pyroxene, and shows an absence of Cr, Ni, and Sc, coupled with a relatively large amount of Zr, Ba, and Rb.

Dolerite-pegmatites. The chemistry of dolerite-pegmatites in general has been

considered recently by WALKER (1953). Examples associated with the main trend (Table 20, cols. 13 and 14) and with the third trend (Table 23, col. 5) have been examined, but none in connection with the iron-rich trend. These pegmatites lie off their associated trends, being richer than usual in iron, and poorer in magnesium and aluminium.

The first example associated with the main trend (Table 20, col. 13) represents one formed at an early stage, as is indicated by its relatively high Cr, V, Ni, Co, and Sc, coupled with low Li, Zr, Sr, and Ba. The other example (Table 20, col. 14) was formed at a relatively late stage, and is much enriched in iron. Here, Cr, V, Ni, Co, and Sc are all low, while Zr, Sr, Ba, and Rb became relatively important.

The pegmatite associated with the third trend (Table 23, col. 5) shows feebler enrichment in iron, in harmony with its association with rocks of this trend. Its stage of development is relatively late, with Cr, Ni, and Co all low, but with moderate amounts of V still present, and relatively high Sc, Y, Zr, Ba, and Rb.

Metasomatic granophyres. These rocks, derived from the surrounding sediments (Table 20, cols. 17 and 18; Table 22, col. 13; and Table 23, col. 7), are associated with the dolerites of all three trends (see Table 20, cols. 15 and 16; Table 22, cols. 10, 11, and 12; Table 23, col. 6). As might be expected, they do not fall on the trends with which they are associated, though there is one exception to this. One of their main features is a relative richness in magnesium, coupled with relative poverty in iron. Their trace element content, too, is peculiar, as may be seen from the figures given in the tables. In other words, they are abnormal rocks, readily distinguishable from normal rocks of the trend with which they are associated. The one exception to this is the rock represented by Table 22, col. 12, from the top of the New Amalfi sheet. This falls perfectly well on the iron-rich trend, and differs considerably in character from the other metasomatic granophyre from the top of the New Amalfi sheet (Table 22, col. 11). Is it possible that this rock is really a magmatic granophyre, like that represented by Table 22, col. 9?

(c) *British Tertiary tholeiitic series (Tables 24–26)*

Of the three chief trends recognizable in these rocks, we had adequate material for only the main trend and the third trend, although a few results of trace element determinations in members of the iron-rich trend will be found in Table 25.

Silicon and Oxygen (Figs. 42e, 42f). The curves for silicon and oxygen in the main trend are very like the curves for these elements in the Karroo main trend, being flat in the earlier stages and steepening in the late-intermediate and late stages. In the third trend, on the other hand, both curves have a fairly steady gradient.

Aluminium and Gallium (Figs. 42e, 42f). The curves for aluminium and gallium are much alike in both trends, except that they are extended at the basic end in the case of the main trend. In both trends Ga follows Al closely, and the average ratio $Ga \times 1000/Al$ is 0.25 for the main trend and 0.26 for the third trend.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, Scandium, and Titanium (Figs. 43e, 43f). The curves for Cr, Mg, and V in the main trend all lie below the corresponding curves for these elements in the third trend; that is, they are being eliminated more rapidly in the former. But Ni and Co behave in

	204.10 ³	227.10 ³	231.10 ³	246.10 ³	238.10 ³	240.10 ³	252.10 ³	243.10 ³	251.10 ³	240.10 ³	246.10 ³	303.10 ³	250.10 ³	253.10 ³	331.10 ³	319.10 ³	339.10 ³	434.10 ³
Si	46.10 ³	78.10 ³	86.10 ³	65.10 ³	58.10 ³	81.10 ³	80.10 ³	81.10 ³	83.10 ³	83.10 ³	87.10 ³	69.10 ³	71.10 ³	74.10 ³	74.10 ³	73.10 ³	73.10 ³	20.10 ³
Al	2.10 ³	2.10 ³	3.10 ³	5.10 ³	5.10 ³	8.10 ³	6.10 ³	8.10 ³	7.10 ³	7.10 ³	13.10 ³	10.10 ³	8.10 ³	16.10 ³	16.10 ³	4.10 ³	4.10 ³	1.10 ³
Ti	8.10 ³	6.10 ³	6.10 ³	2.10 ³	5.10 ³	8.10 ³	6.10 ³	8.10 ³	2.10 ³	2.10 ³	8.10 ³	6.10 ³	14.10 ³	16.10 ³	16.10 ³	1.10 ³	1.10 ³	—
Mg	166.10 ³	88.10 ³	71.10 ³	62.10 ³	43.10 ³	46.10 ³	35.10 ³	39.10 ³	34.10 ³	20.10 ³	20.10 ³	7.10 ³	35.10 ³	16.10 ³	0.10 ³	14.10 ³	10.10 ³	—
Fe	100.10 ³	75.10 ³	73.10 ³	86.10 ³	82.10 ³	75.10 ³	72.10 ³	83.10 ³	84.10 ³	86.10 ³	86.10 ³	86.10 ³	88.10 ³	114.10 ³	80.10 ³	36.10 ³	26.10 ³	7.10 ³
Na	5.10 ³	10.10 ³	12.10 ³	18.10 ³	34.10 ³	17.10 ³	15.10 ³	19.10 ³	13.10 ³	19.10 ³	21.10 ³	23.10 ³	17.10 ³	13.10 ³	29.10 ³	20.10 ³	24.10 ³	3.10 ³
Ca	33.10 ³	61.10 ³	66.10 ³	78.10 ³	81.10 ³	73.10 ³	79.10 ³	71.10 ³	67.10 ³	65.10 ³	56.10 ³	29.10 ³	61.10 ³	54.10 ³	14.10 ³	11.10 ³	17.10 ³	2.10 ³
K	3.10 ³	4.10 ³	4.10 ³	4.10 ³	5.10 ³	5.10 ³	5.10 ³	6.10 ³	8.10 ³	16.10 ³	14.10 ³	31.10 ³	8.10 ³	12.10 ³	23.10 ³	33.10 ³	17.10 ³	14.10 ³
P	(305)	(305)	(tr.)	(305)	(700)	(tr.)	(830)	(610)	(700)	(830)	(2010)	(940)	(1200)	(1005)	(395)	(525)	(610)	(tr.)
Ga	10	20	30	30	20	20	30	30	25	20	30	30	25	30	20	30	30	<5
Cr	2000	1000	800	650	275	250	270	150	150	230	200	150	125	10	35	55	55	*
V	150	150	150	125	250	400	250	250	150	230	200	150	125	10	35	60	70	*
Li	5	5	10	5	10	5	5	10	15	30	30	35	5	10	30	50	50	1
Co	250	300	225	30	10	100	85	70	15	20	20	20	125	7	7	6	20	*
Ni	80	70	15	30	45	55	45	45	25	25	15	20	40	7	5	8	8	*
Sc	*	15	10	30	40	45	45	35	30	30	15	20	50	7	5	6	8	*
Zr	40	50	90	35	100	100	100	100	125	125	250	250	35	125	200	125	100	*
Mn	(1240)	(tr.)	(1705)	(1470)	(1860)	(1860)	(1085)	(1705)	(1085)	(620)	(3410)	(1005)	(3330)	(3175)	(230)	(310)	(230)	200
Y	*	10	15	10	20	20	25	25	25	30	35	45	*	250	25	20	20	(tr.)
Sr	50	80	80	100	270	200	100	150	200	350	200	300	100	250	200	225	200	*
Pb	50	80	80	100	270	200	100	150	200	350	200	300	100	250	200	225	200	*
Ba	90	100	100	50	250	225	100	150	450	350	400	1000	85	750	1200	900	800	200
Rb	90	100	100	50	250	225	100	150	450	350	400	1000	85	750	1200	900	800	200
Fe	39	49	53	57	67	64	69	70	72	82	82	90	74	89	78	75	73	99+
Mg	61	51	47	43	33	36	31	30	28	18	18	10	26	11	22	25	27	1-
Fe	38	46	47	50	59	55	59	59	61	64	63	50	63	77	33	39	35	29
Alk	3	7	10	11	12	15	15	16	15	23	23	44	15	14	10	13	13	29
Position	-12.8	-7.0	-5.6	-5.4	-4.1	-3.4	-2.5	-2.3	-0.9	+1.1	+1.9	+9.6	-0.5	+2.6	+11.2	+11.4	+10.3	+15.7

Table 20a. Karoo dolerites: main trend

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Ga × 1000/Al	0.22	0.26	0.12	0.46	0.24	0.25	0.37	0.37	0.30	0.24	0.34	0.29	0.35	0.49	0.27	0.26	0.41	—
Cr × 1000/Mg	12.0	11.4	11.3	10.5	6.4	5.4	7.7	3.8	4.7	1.0	0.7	0.7	7.1	*	2.2	3.9	5.5	—
V × 1000/Mg	0.9	1.7	2.1	2.0	5.8	8.7	0.1	0.4	4.4	11.5	9.5	21.4	3.6	0.6	3.9	4.3	7.0	—
Li × 1000/Mg	0.03	0.1	0.1	0.1	0.2	0.1	0.1	0.3	0.4	1.5	1.4	5.0	0.1	0.6	3.9	3.6	5.0	—
Ni × 1000/Mg	1.5	3.4	3.2	1.1	2.1	2.2	2.4	1.8	0.7	1.0	0.7	0.7	3.6	0.8	0.8	0.6	2.0	—
Co × 1000/Mg	0.5	0.8	0.8	0.5	1.0	1.2	1.3	1.2	0.7	1.2	1.0	2.9	1.1	0.4	0.6	0.4	0.8	—
Fe/Mg	0.7	1.0	1.1	1.3	2.0	1.8	2.2	2.3	2.5	4.7	4.4	9.0	2.9	8.4	3.4	3.1	2.7	—
Cr × 1000/Fe	18.5	11.6	10.1	7.9	3.2	3.0	3.5	1.6	1.9	0.2	0.2	0.1	2.5	*	0.6	1.3	2.0	—
V × 1000/Fe	1.4	1.7	1.9	1.5	2.9	4.8	3.2	2.7	1.7	2.4	2.2	2.4	1.2	0.1	1.1	1.4	2.6	—
Co × 1000/Fe	0.7	0.8	0.8	0.4	0.5	0.7	0.6	0.5	0.3	0.3	0.2	0.3	0.4	0.05	0.2	0.1	0.3	—
Y × 1000/Ca	*	0.2	0.2	0.1	0.2	0.3	0.3	0.4	0.4	0.5	0.6	1.6	*	0.6	1.8	1.8	1.2	*
Sr × 100/Ca	0.2	0.1	0.1	0.1	0.3	0.3	0.1	0.2	0.3	0.5	0.4	1.0	0.2	0.5	1.4	2.0	1.2	*
Sr × 100/Ca + K	0.1	0.1	0.1	0.1	0.3	0.3	0.1	0.2	0.3	0.4	0.3	0.5	0.1	0.4	0.5	0.5	0.6	*
Ba × 100/K	3.0	3.3	2.5	1.3	6.2	4.5	2.0	2.5	5.6	2.2	2.9	3.2	1.1	6.2	4.8	2.7	4.7	1.4
Rb × 100/K	*	*	*	*	0.2	0.1	*	0.2	0.6	0.5	1.1	0.6	*	1.0	0.3	0.7	1.2	0.3

[Analysis numbers given below are those of Table 15 in WALKER and POIDEVIAERT, 1949]

1. Pictite [accumulative] (anal. 42).
2. Dolerite (Kokstad type) [accumulative] (anal. 13).
3. Dolerite (Kokstad type) [accumulative] (anal. 14).
4. Dolerite (Kokstad type) [accumulative] (anal. 25).
5. Dolerite (Perdekloof type) (anal. 1).
6. Dolerite (Perdekloof type) (anal. 4).
7. Dolerite (Blauwkrans type) (anal. 12).
8. Dolerite (Perdekloof type) (anal. 5).
9. Chilled basalt (anal. 61).
10. Dolerite (Kentani type) (anal. 37).
11. Dolerite (Kentani type) (anal. 36).
12. Acid rock. Thomas River (anal. 85).
13. Dolerite-pegmatite (anal. 67).
14. Dolerite-pegmatite (anal. 65).
15. Metasomatic granophyre, Rietkop (anal. 96).
16. Metasomatic granophyre, Rietkop (anal. 95).
17. Ecra Siltstone, Rietkop (anal. 101).
18. Molteno grit, Malmkwe Poort (anal. 113).

the opposite way, and the curves for these two elements in the main trend lie, in general, slightly above those in the third trend.

The Fe curve shows a feeble maximum in the intermediate stage of the main trend, but there is no trace of this in the Fe curve of the third trend, which lies below that of the main trend throughout. It will be noted that there is here apparently no trace of a maximum on the V curve in the main trend corresponding with the feeble one observed for Fe.

Karoo dolerites: Mt. Arthur tholeiites

Table 21

	1	2	3	4	5
Si	249.10 ³	245.10 ³	253.10 ³	246.10 ³	253.10 ³
Al	78.10 ³	81.10 ³	73.10 ³	76.10 ³	75.10 ³
Ti	3.10 ³	7.10 ³	5.10 ³	7.10 ³	10.10 ³
Fe ^{'''}	12.10 ³	15.10 ³	13.10 ³	20.10 ³	27.10 ³
Mg	44.10 ³	41.10 ³	38.10 ³	37.10 ³	30.10 ³
Fe ^{''}	65.10 ³	66.10 ³	77.10 ³	73.10 ³	69.10 ³
Na	15.10 ³	15.10 ³	16.10 ³	24.10 ³	18.10 ³
Ca	80.10 ³	76.10 ³	72.10 ³	65.10 ³	59.10 ³
K	5.10 ³	4.10 ³	7.10 ³	7.10 ³	9.10 ³
P	(tr.)	(tr.)	(tr.)	(tr.)	(395)
Ga	20	20	25	25	25
Cr	250	250	50	100	40
V	300	200	175	225	150
Li	5	10	20	15	15
Ni	50	50	30	30	15
Co	45	25	30	30	20
Sc	60	50	40	40	20
Zr	70	80	65	100	80
Mn	(1780)	(2480)	(1625)	(2555)	(2015)
Y	25	15	20	25	25
Sr	220	150	150	200	150
Pb	*	*	*	*	*
Ba	150	200	175	225	200
Rb	*	710	15	40	45
Fe	64	66	70	72	76
Mg	36	34	30	28	24
Fe	55	58	60	58	62
Mg	31	29	25	23	20
Alk	14	13	15	19	18
Position	-3.6	-3.1	-1.9	-1.2	+0.4

Table 21a

	1	2	3	4	5
Ga × 1000/Al	0.26	0.25	0.34	0.33	0.33
Cr × 1000/Mg	5.7	6.1	1.3	2.7	1.3
V × 1000/Mg	6.8	4.9	4.6	6.1	5.0
Li × 1000/Mg	0.1	0.2	0.5	0.4	0.5
Ni × 1000/Mg	1.1	1.2	0.8	0.8	0.5
Co × 1000/Mg	1.0	0.6	0.8	0.8	0.7
Fe/Mg	1.7	2.0	2.4	2.5	3.2
Cr × 1000/Fe	3.2	3.1	0.6	1.1	0.4
V × 1000/Fe	3.9	2.5	1.9	2.4	1.6
Co × 1000/Fe	0.6	0.3	0.3	0.3	0.2
Y × 1000/Ca	0.3	0.2	0.3	0.4	0.4
Sr × 100/Ca	0.3	0.2	0.2	0.3	0.3
Sr × 100/Ca + K	0.3	0.2	0.2	0.3	0.2
Ba × 100/K	3.0	5.0	2.5	3.2	2.2
Rb × 100/K	*	0.2	0.2	0.6	0.5

[Analysis numbers given below are those of Table 15 in WALKER and POLDERVAART, 1949]

1. Farm Ashton (anal. 74).
2. Farm Falloden (anal. 71).
3. Farm Glencoe (anal. 77).
4. Farm Falloden (anal. 72).
5. Farm Watershed (anal. 76).

There is a tendency in both trends towards a small but steady enrichment in Li as the value of the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ rises. Once again, Ti passes through a maximum in harmony with Fe in the main trend (as it does also in the iron-rich trend). Sc decreases in amount as the function $[(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ rises in value, and falls below the limit of sensitivity in the extreme acid members of all three trends.

With the exception of Ni, Co, and V, the behaviour of the elements in the main trend here is very similar to that in the main trend of the Karroo dolerites.

Calcium and Strontium (Figs. 44e, 44f). The curves for both elements are practically identical in both trends. Once more, Sr is low in value throughout, but tends to pass through a feeble maximum in the intermediate stages.

Yttrium is present throughout, and tends to increase in amount towards the acid end of each trend.

Sodium (Fig. 44e, 44f). The curves for Na are of much the same general form in both trends, but that for the main trend lies above that for the third trend in the

Table 22. Karoo dolerites: iron-rich trend

	1	2	3	4	5	6	7	8	9	10	11	12	13
Si	201.10 ³	201.10 ³	229.10 ³	237.10 ³	239.10 ³	244.10 ³	254.10 ³	248.10 ³	302.10 ³	290.10 ³	296.10 ³	294.10 ³	363.10 ³
Al	32.10 ³	38.10 ³	84.10 ³	88.10 ³	88.10 ³	83.10 ³	78.10 ³	66.10 ³	62.10 ³	67.10 ³	75.10 ³	57.10 ³	66.10 ³
Ti	5.10 ³	3.10 ³	4.10 ³	5.10 ³	8.10 ³	5.10 ³	9.10 ³	19.10 ³	8.10 ³	8.10 ³	9.10 ³	9.10 ³	1.10 ³
Fe ⁺⁺⁺	12.10 ³	4.10 ³	2.10 ³	4.10 ³	3.10 ³	14.10 ³	6.10 ³	25.10 ³	12.10 ³	2.10 ³	8.10 ³	26.10 ³	10.10 ³
Mg	190.10 ³	188.10 ³	59.10 ³	44.10 ³	47.10 ³	35.10 ³	29.10 ³	16.10 ³	4.10 ³	28.10 ³	11.10 ³	4.10 ³	1.10 ³
Fe ⁺⁺	84.10 ³	98.10 ³	68.10 ³	75.10 ³	76.10 ³	77.10 ³	88.10 ³	101.10 ³	69.10 ³	62.10 ³	51.10 ³	73.10 ³	12.10 ³
Na	5.10 ³	4.10 ³	10.10 ³	12.10 ³	14.10 ³	14.10 ³	19.10 ³	15.10 ³	22.10 ³	15.10 ³	38.10 ³	22.10 ³	16.10 ³
Ca	34.10 ³	27.10 ³	99.10 ³	89.10 ³	71.10 ³	78.10 ³	61.10 ³	61.10 ³	31.10 ³	54.10 ³	29.10 ³	36.10 ³	2.10 ³
K	1.10 ³	2.10 ³	3.10 ³	1.10 ³	5.10 ³	5.10 ³	7.10 ³	8.10 ³	25.10 ³	8.10 ³	16.10 ³	22.10 ³	32.10 ³
P	(175)	(tr.)	(525)	(305)	(655)	(830)	(525)	(1005)	(830)	(395)	(480)	(1485)	(tr.)
Ga	5	7	30	30	25	20	30	30	25	25	20	30	25
Cr	1500	2000	*	425	400	400	5	*	*	125	35	*	*
V	80	100	300	220	175	300	200	200	75	100	60	*	170
Li	5	3	10	5	5	8	10	15	35	15	10	25	15
Ni	750	1000	*	150	125	95	25	5	35	35	*	*	5
Co	70	80	35	50	30	45	30	25	8	15	7	*	20
Sc	*	*	*	20	30	40	40	*	*	25	70	*	*
Zr	20	25	200	65	65	90	100	100	400	70	125	200	100
Mn	(1860)	(1550)	(tr.)	(540)	(1705)	(930)	(1470)	(2015)	(1395)	(1240)	(1005)	(1780)	(tr.)
Y	*	*	30	20	20	20	25	25	85	20	30	50	20
Sr	30	40	100	125	150	150	175	120	200	100	325	100	150
Pb	*	*	*	*	*	*	*	*	*	*	*	*	*
Ba	50	55	200	70	125	250	225	325	1000	250	800	800	300
Rb	*	*	50	*	10	10	15	40	125†	40	85	150	40
Fe	34	35	54	64	63	72	76	89	95	70	84	96	96
Mg	66	65	46	36	37	28	24	11	5	30	16	4	4
Fe	33	34	50	58	55	63	64	76	61	56	47	67	31
Mg	65	64	42	32	32	24	19	10	3	24	9	3	1
Alk	2	2	8	10	13	13	17	14	36	20	44	30	68
Position	-15.6	-14.6	-8.0	-5.3	-3.3	-2.7	+0.2	+1.4	+9.1	+2.3	+7.5	+8.0	+15.0

† Also Mo2, La 60 p.p.m.

Table 22a. Karoo dolerites: iron-rich trend

	1	2	3	4	5	6	7	8	9	10	11	12	13
Ga × 1000/Al	0.16	0.19	0.36	0.34	0.28	0.24	0.38	0.45	0.40	0.37	0.27	0.53	0.38
Cr × 1000/Mg	8.0	10.6	*	9.1	8.5	11.4	0.2	*	*	4.5	3.2	*	*
V × 1000/Mg	0.4	0.5	5.1	5.0	3.7	8.6	6.9	12.5	1.2	3.6	5.5	*	170.0
Li × 1000/Mg	0.03	0.02	0.2	0.1	0.1	0.2	0.3	0.9	8.8	0.5	0.9	6.2	15.0
Ni × 1000/Mg	4.0	5.3	*	3.4	2.7	2.7	0.9	0.3	*	1.2	*	*	5.0
Co × 1000/Mg	0.4	0.4	0.6	1.1	0.6	1.3	1.0	1.6	2.0	0.5	0.6	*	20.0
Fe/Mg	0.5	0.5	1.2	1.8	1.7	2.6	3.2	7.9	20.2	2.3	5.4	24.7	22.0
Cr × 1000/Fe	15.6	19.6	*	5.1	5.1	4.4	0.05	*	*	2.0	0.6	*	*
V × 1000/Fe	0.8	1.0	4.3	2.8	2.2	3.3	2.1	1.6	0.06	1.6	1.0	*	7.7
Co × 1000/Fe	0.7	0.8	0.5	0.6	0.4	0.5	0.3	0.2	0.1	0.2	0.1	*	0.9
Y × 1000/Ca	*	*	0.3	0.2	0.3	0.3	0.4	0.4	2.7	0.4	1.0	1.4	10.0
Sr × 100/Ca	0.1	0.1	0.1	0.1	0.2	0.2	0.3	0.2	0.6	0.2	1.1	0.3	7.5
Sr × 100/Ca + K	0.1	0.1	0.1	0.1	0.2	0.2	0.3	0.2	0.4	0.2	0.7	0.2	0.4
Ba × 100/K	5.0	2.8	6.7	7.0	2.5	5.0	3.2	4.1	4.0	3.1	5.0	3.6	0.9
Rb × 100/K	*	*	1.7	*	0.2	0.2	0.2	0.5	0.5	0.5	0.5	0.7	0.1

Analysis numbers given below are those of Table 15 in WALKER and POLDERVAART, 1949]

1. Picrite [accumulative] Elephant's Head dyke (anal. 40).
2. Picrite [accumulative] Elephant's Head dyke (anal. 41).
3. Dolerite (Kokstad type) [accumulative] Elephant's Head dyke (anal. 15).
4. Dolerite (Kokstad type). Execution Rock (anal. 17).
5. Dolerite (Kokstad type) (anal. 18).
6. Dolerite (Blaauwkrans type) (anal. 9).
7. New Amalfi sheet, 100' below upper contact (anal. 53).

8. New Amalfi sheet, 50' below upper contact (anal. 54).
9. New Amalfi sheet, 2' below upper contact (anal. 55).
10. Metasomatic granophyre, Elephant's Head dyke, margin (anal. 91).
11. Metasomatic granophyre, New Amalfi sheet, top (anal. 93).
12. Metasomatic granophyre, New Amalfi sheet, top (anal. 92).
13. Centre of xenolith of Burgersdorp sandstone near upper contact of New Amalfi sheet (anal. 108).

Table 23. Karoo dolerites: third trend

	1	2	3	4	5	6	7
Si	242.10 ³	250.10 ³	244.10 ³	251.10 ³	274.10 ³	311.10 ³	330.10 ³
Al	83.10 ³	85.10 ³	85.10 ³	80.10 ³	78.10 ³	81.10 ³	80.10 ³
Ti	5.10 ³	4.10 ³	6.10 ³	7.10 ³	7.10 ³	3.10 ³	2.10 ³
Fe'''	8.10 ³	9.10 ³	4.10 ³	7.10 ³	18.10 ³	8.10 ³	6.10 ³
Mg	49.10 ³	44.10 ³	47.10 ³	44.10 ³	19.10 ³	13.10 ³	11.10 ³
Fe''	67.10 ³	64.10 ³	69.10 ³	70.10 ³	65.10 ³	40.10 ³	31.10 ³
Na	12.10 ³	11.10 ³	18.10 ³	16.10 ³	15.10 ³	21.10 ³	13.10 ³
Ca	80.10 ³	74.10 ³	71.10 ³	68.10 ³	52.10 ³	18.10 ³	9.10 ³
K	5.10 ³	5.10 ³	8.10 ³	6.10 ³	13.10 ³	29.10 ³	29.10 ³
P	(260)	(480)	(400)	(830)	(1355)	(875)	(700)
Ga	20	20	25	25	30	30	15
Cr	400	300	500	500	20	55	20
V	200	250	125	125	85	60	25
Li	10	10	6	5	15	50	15
Ni	70	90	5	5	*	10	10
Co	30	45	25	30	15	10	5
Sc	35	40	35	20	50	?10	*
Zr	80	90	80	100	225	125	150
Mn	(1395)	(1935)	(540)	(1005)	(1005)	(310)	(930)
Y	25	20	25	20	40	25	20
Sr	125	200	200	100	125	575	300
Pb	*	*	*	*	*	*	?10
Ba	175	225	250	175	750	900	650
Rb	20	10	15	15	150	165	60
Fe	60	62	61	64	81	79	77
Mg	40	38	39	36	19	21	23
Fe	53	55	50	54	63	43	41
Mg	35	33	32	31	15	12	12
Alk	12	12	18	15	22	45	47
Position	-4.3	-3.0	-2.9	-2.2	+3.3	+10.2	+11.9

Table 23a. Karoo dolerites: third trend

	1	2	3	4	5	6	7
Ga × 1000/Al	0.24	0.24	0.29	0.31	0.38	0.37	0.19
Cr × 1000/Mg	8.2	6.8	10.6	11.4	1.1	4.2	1.8
V × 1000/Mg	4.1	5.7	2.7	2.8	4.5	4.6	2.3
Li × 1000/Mg	0.2	0.2	0.1	0.1	0.8	3.8	1.4
Ni × 1000/Mg	1.4	2.0	0.1	0.1	*	0.8	0.9
Co × 1000/Mg	0.6	1.0	0.5	0.7	0.8	0.8	0.5
Fe/Mg	1.5	1.7	1.6	1.7	4.4	3.7	3.4
Cr × 1000/Fe	5.3	4.1	6.8	6.5	0.2	1.1	0.5
V × 1000/Fe	2.7	3.4	1.7	1.6	1.0	1.3	0.7
Co × 1000/Fe	0.4	0.6	0.3	0.4	0.2	0.2	0.1
Y × 1000/Ca	0.3	0.3	0.4	0.3	0.8	1.4	2.2
Sr × 100/Ca	0.15	0.3	0.3	0.15	0.2	3.2	3.3
Sr × 100/Ca + K	0.15	0.3	0.3	0.15	0.2	1.2	0.8
Ba × 100/K	3.5	4.5	3.1	2.9	5.8	3.1	2.2
Rb × 100/K	0.4	0.2	0.2	0.3	1.2	0.6	0.2

Analysis numbers given below are those of Table 15 in
WALKER and POLDERVAART, 1949]

1. Dolerite (Hanover type) (anal. 33).

2. Dolerite (Hangnest type) (anal. 26).

3. Dolerite (Hanover type) (anal. 34).

4. Dolerite (Hangnest type) (anal. 27).

5. Dolerite-pegmatite, Hangnest (anal. 70).

6. Metasomatic granophyre, Hangnest (anal. 94).

7. Beaufort Siltstone, Hangnest (anal. 104).

Figs. 44a-i. Variation in calcium, strontium, barium, sodium, rubidium and potassium. Values in weight per cent with Sr, Ba, and Rb $\times 100$.

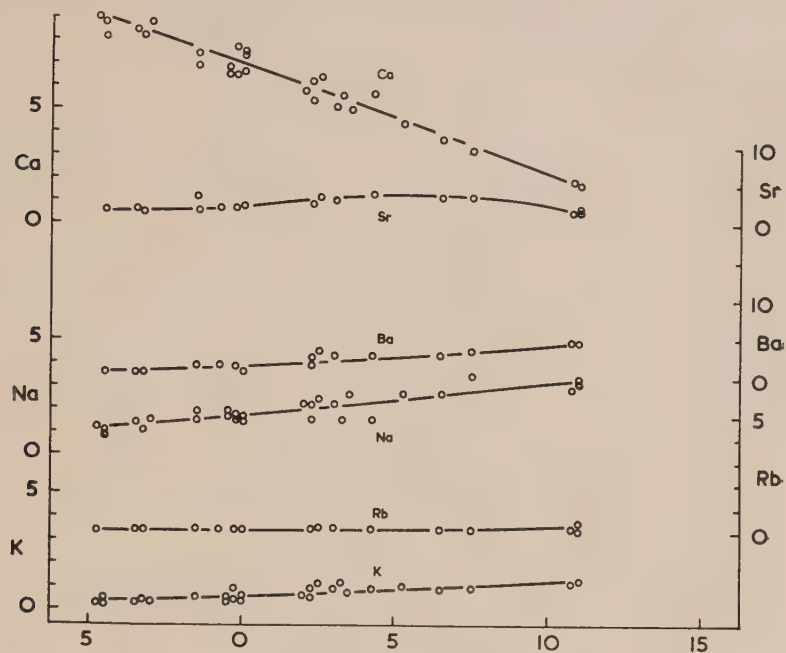


Fig. 44a. Hakone P-series.

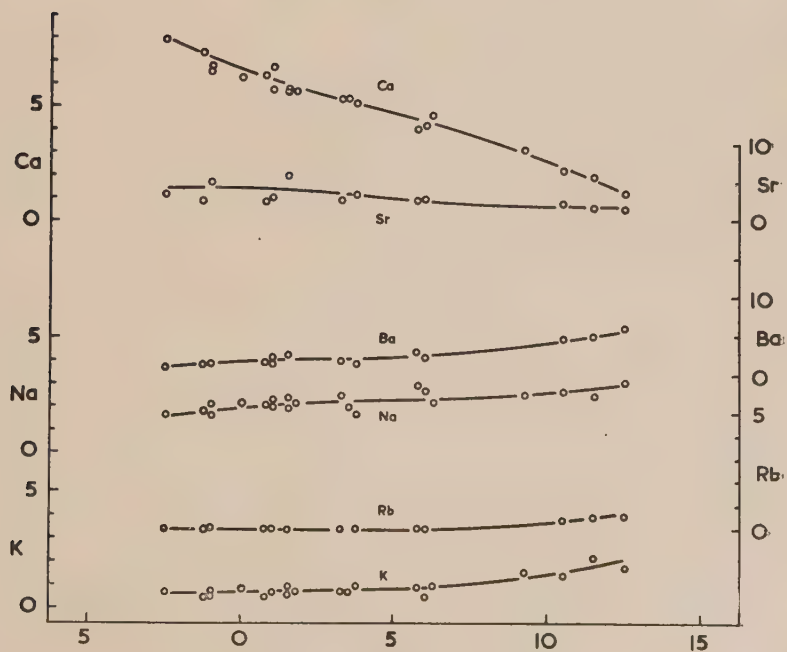


Fig. 44b. Hakone H-series.

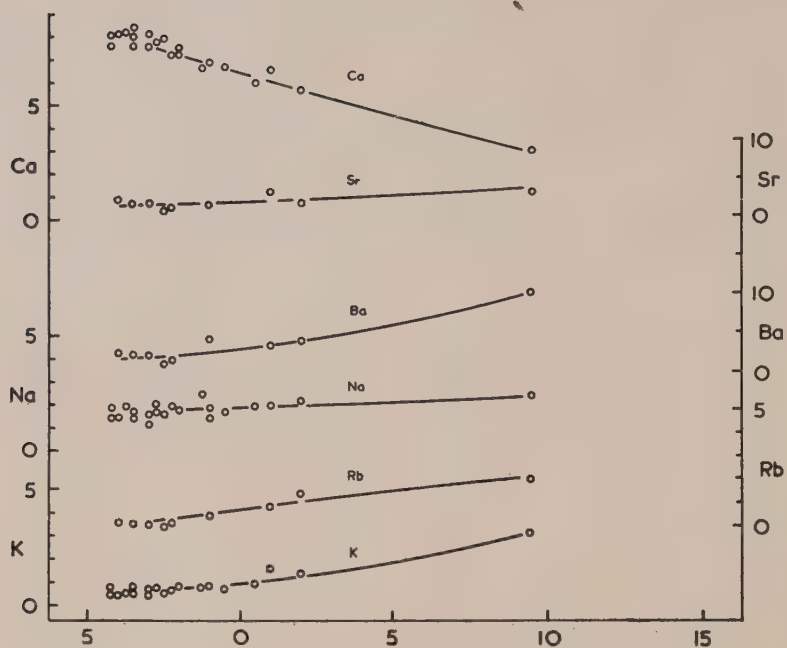


Fig. 44c. Karroo main trend.

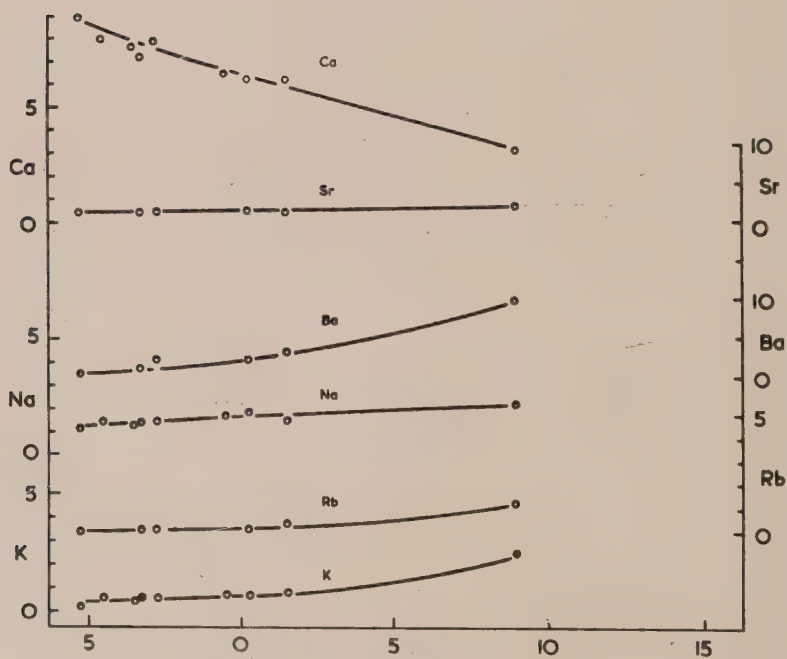


Fig. 44d. Karroo iron-enriched trend.

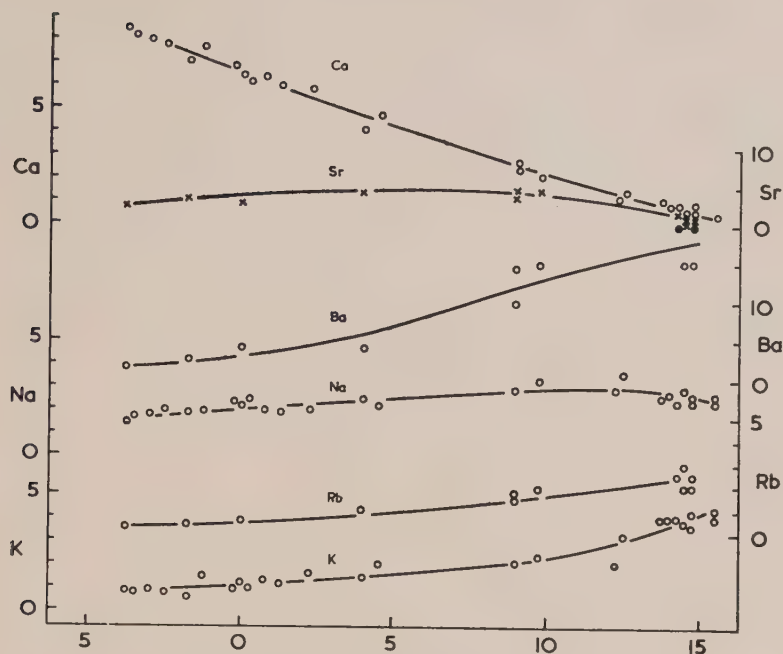


Fig. 44e. British Tertiary main trend.

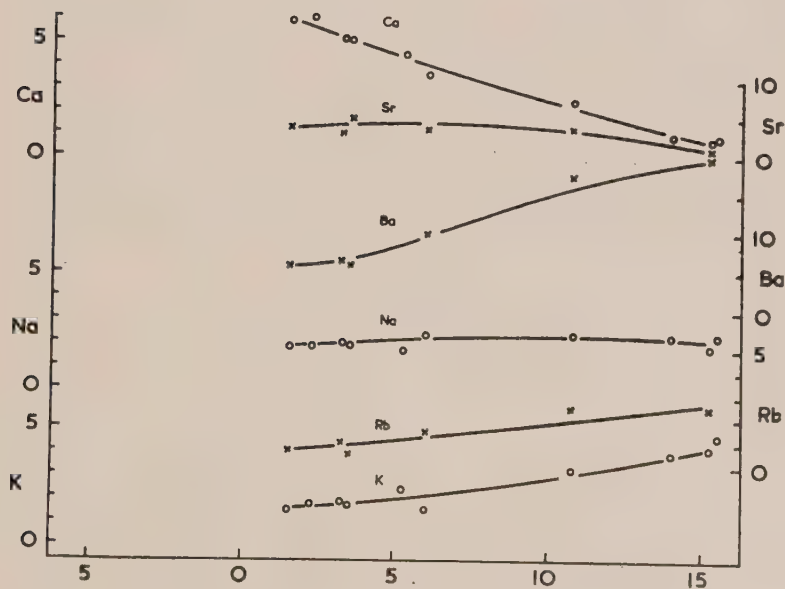


Fig. 44f. British Tertiary third trend.

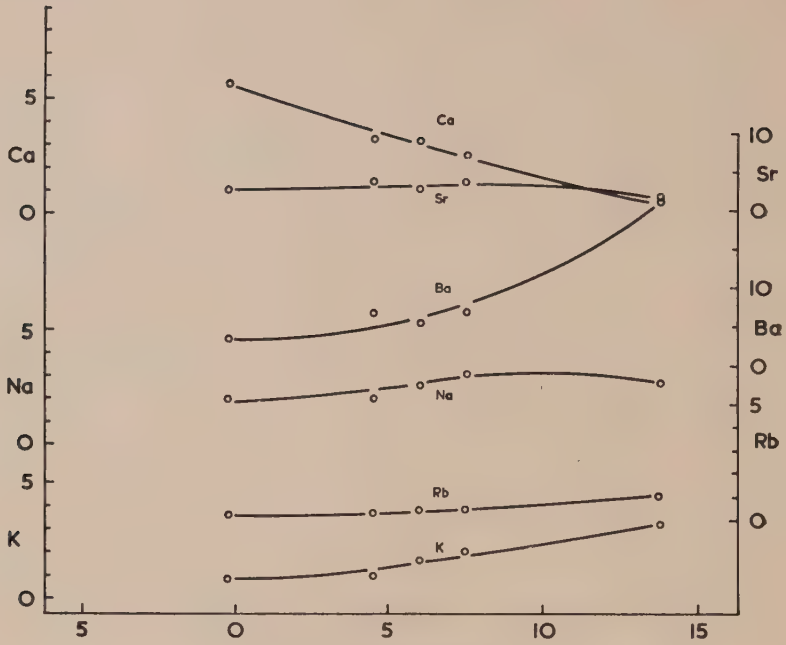


Fig. 44g. Northfield sill.

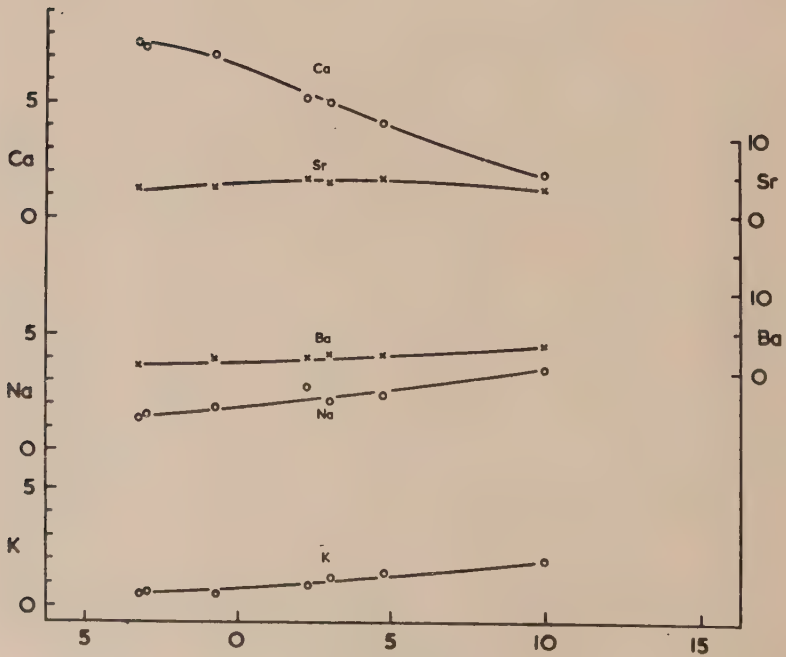


Fig. 44h. Dillsburg sill.

intermediate and late stages. It passes through a maximum at a late stage and then falls slightly.

Potassium, Barium, Rubidium, and Lead (Figs. 44e, 44f). The curves for K behave in a way opposite to those for Na, the curve for K in the third trend lying slightly above that for the main trend. In sympathy with this, the curves for Ba and Rb in the third trend also lie slightly above the curves for the same elements

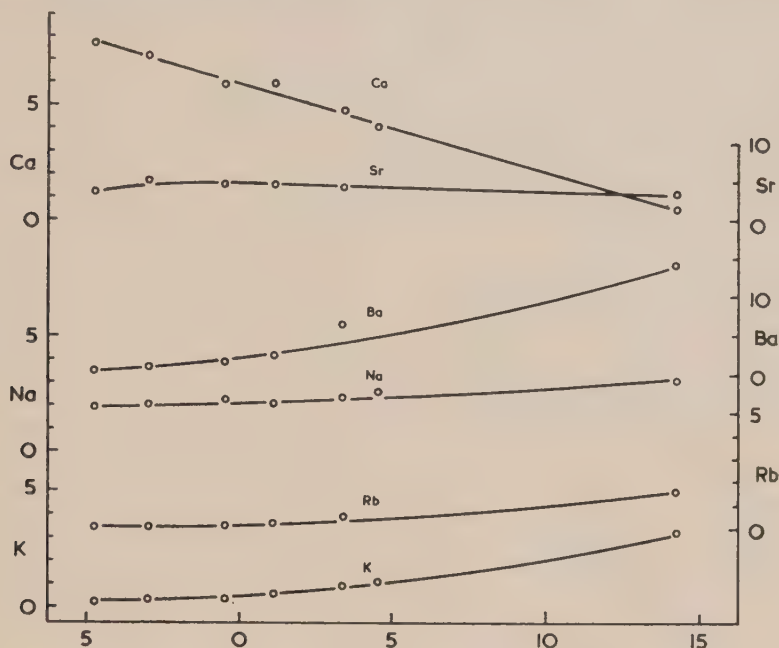


Fig. 44i. Skaergaard intrusion.

in the main trend, though the form of the curves is similar. Lead first appears above the limit of sensitivity in the intermediate members of the main trend, and thereafter rises in amount. It behaves similarly in the third trend.

Zirconium, in both trends, increases in amount for a time and then tends to remain more or less constant.

The parental magma of both these trends (and of the iron-rich trend, too) is believed to be represented by the extreme basic end-member of the main trend, as the curves for the major and minor elements in the third trend would, if extended, pass almost exactly through the points representing this basic end-member.

(d) *The Northfield Sill (Table 27)*

Silicon and Oxygen (Fig. 42g). The curves for silicon and oxygen have the same shape and inclination as those of the Hakone H-series, but lie below the latter.

Aluminium and Gallium (Fig. 42g). The curves for aluminium and gallium correspond closely with those of the Scottish tholeiitic main and third trends, as far as they go. The average ratio $Ga \times 1000/Al$ is 0.29.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, Scandium, and Titanium (Fig. 43g). The curves for Mg, Fe, and Co decline steadily as the value

Table 24. British Tertiary tholeiitic: main trend

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Si	240.10 ³	250.10 ³	243.10 ³	262.10 ³	308.10 ³	310.10 ³	311.10 ³	345.10 ³	347.10 ³	343.10 ³	342.10 ³	356.10 ³	226.10 ³	226.10 ³	234.10 ³
Al	79.10 ³	86.10 ³	70.10 ³	72.10 ³	72.10 ³	68.10 ³	78.10 ³	70.10 ³	69.10 ³	66.10 ³	64.10 ³	63.10 ³	107.10 ³	101.10 ³	100.10 ³
Ti	7.10 ³	8.10 ³	17.10 ³	17.10 ³	7.10 ³	7.10 ³	5.10 ³	3.10 ³	2.10 ³	2.10 ³	2.10 ³	2.10 ³	6.10 ³	4.10 ³	4.10 ³
Fe ⁺⁺	13.10 ³	15.10 ³	29.10 ³	24.10 ³	8.10 ³	13.10 ³	9.10 ³	3.10 ³	6.10 ³	15.10 ³	15.10 ³	8.10 ³	14.10 ³	4.10 ³	23.10 ³
Mg	42.10 ³	36.10 ³	29.10 ³	22.10 ³	7.10 ³	7.10 ³	9.10 ³	2.10 ³	18.10 ³	6.10 ³	6.10 ³	1.10 ³	33.10 ³	32.10 ³	38.10 ³
Mg	66.10 ³	68.10 ³	69.10 ³	66.10 ³	50.10 ³	47.10 ³	35.10 ³	16.10 ³	12.10 ³	13.10 ³	16.10 ³	8.10 ³	51.10 ³	33.10 ³	58.10 ³
Ca	15.10 ³	19.10 ³	22.10 ³	25.10 ³	28.10 ³	27.10 ³	33.10 ³	27.10 ³	25.10 ³	29.10 ³	24.10 ³	25.10 ³	13.10 ³	13.10 ³	13.10 ³
Na	84.10 ³	70.10 ³	64.10 ³	41.10 ³	26.10 ³	27.10 ³	21.10 ³	8.10 ³	9.10 ³	6.10 ³	9.10 ³	6.10 ³	94.10 ³	86.10 ³	75.10 ³
K	7.10 ³	5.10 ³	12.10 ³	15.10 ³	20.10 ³	21.10 ³	24.10 ³	38.10 ³	40.10 ³	39.10 ³	44.10 ³	36.10 ³	8.10 ³	2.10 ³	4.10 ³
P	(700)	(600)	(1300)	(1300)	(1300)	(1300)	(900)	(700)	(400)	(400)	(400)	(900)	(175)	(1300)	(400)
Ga	20	20	20	15	20	20	20	15	15	15	15	15	20	20	20
Cr	250	50	65	50	25	30	25	10	10	25	35	20	250	90	170
V	275	150	200	125	25	30	25	30	30	30	35	20	200	100	100
Li	60	40	40	20	15	15	5	5	5	5	5	5	150	20	100
Ni	60	40	40	20	15	15	5	5	5	5	5	5	150	20	100
Ni	55	45	50	40	5	5	5	5	5	5	5	5	50	45	45
Co	55	45	50	40	5	5	5	5	5	5	5	5	50	45	45
Co	40	35	25	25	10	10	10	10	10	10	10	10	10	10	20
Sc	40	35	25	25	10	10	10	10	10	10	10	10	10	10	20
Zr	80	100	200	170	225	300	300	250	200	350	300	250	100	30	100
Mn	(1470)	(1400)	(2000)	(3000)	(2000)	(1500)	(2000)	(400)	(150)	(1500)	(1500)	(1500)	(2300)	(2300)	(2000)
Zn	20	35	20	40	25	30	50	50	60	30	35	55	250	350	400
Y	200	300	250	400	350	425	450	150	100	30	125	100	250	350	400
Sr	200	300	250	400	350	425	450	150	100	30	125	100	250	350	400
Pb	200	300	250	400	350	425	450	150	100	30	125	100	250	350	400
Ba	170	250	400	400	1000	1500	1500	2000	2000	1500	2000	1500	100	60	20
Rb	20	30	50	100	175	150	150	250	300	200	250	200	50	60	20
Fe	65	67	77	80	89	90	83	90	91	98	98	94	66	70	67
Mg	35	33	23	20	11	10	17	10	9	2	2	6	34	30	33
Fe	55	55	61	60	52	52	39	22	21	29	31	21	54	59	60
Mg	29	27	18	14	6	6	8	2	2	0.5	0.5	1	28	25	28
Alk	16	18	21	26	42	42	53	76	77	70.5	68.5	73	18	16	12
Position	-3.8	-1.3	0.0	+3.9	+9.0	+9.0	+9.8	+14.3	+14.5	+14.6	+14.8	+14.8	-4.4	-4.1	-3.2

Table 24a. British Tertiary tholeiitic: main trend

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ga × 1000/Al	0.25	0.23	0.29	0.21	0.28	0.29	0.26	0.21	0.22	0.23	0.23	0.24	0.28	0.20	0.20
Cr × 1000/Mg	6.0	1.4	2.2	2.3	0.4	0.4	0.6	*	*	*	*	*	7.6	2.8	2.2
V × 1000/Mg	6.5	4.2	6.9	6.7	3.6	4.3	2.8	5.0	5.6	*	*	*	6.1	3.1	4.4
Li × 1000/Mg	0.5	1.1	1.4	1.4	0.7	2.1	0.6	15.0	16.7	42.0	58.0	20.0	1.5	0.6	0.8
Ni × 1000/Mg	1.4	1.2	1.7	1.8	0.7	0.7	1.1	*	*	*	*	*	4.5	1.4	2.6
Co × 1000/Mg	1.3	0.8	1.6	1.1	0.7	0.7	0.7	9.5	10.0	47.0	52.0	16.0	1.5	1.2	1.2
Fe/Mg	1.9	2.0	3.3	4.1	8.3	8.6	4.8	0.1	0.1	0.1	0.1	0.1	2.0	2.4	2.1
Cr × 1000/Fe	3.2	0.7	0.7	0.6	0.1	0.1	0.1	*	*	*	*	*	3.8	1.2	1.0
V × 1000/Fe	3.5	2.1	2.1	1.4	0.4	0.3	0.6	0.5	0.6	*	*	*	3.1	1.3	2.1
Co × 1000/Fe	0.7	0.4	0.5	0.3	0.1	0.1	*	0.1	0.1	*	*	*	0.3	0.5	0.6
Y × 1000/Ca	0.2	0.5	0.3	1.0	1.0	1.1	2.4	6.2	6.7	5.0	3.9	9.2	*	*	0.3
Sr × 100/Ca	0.2	0.4	0.6	1.0	1.3	1.6	2.1	1.9	1.9	0.8	1.4	1.7	0.3	0.4	0.5
Sr × 100/Ca + K	0.2	0.4	0.7	1.0	0.8	0.9	1.0	0.3	0.2	0.1	0.2	0.2	0.2	0.4	0.5
Ba × 100/K	2.4	5.0	3.3	2.7	5.0	7.1	6.2	5.3	5.0	3.8	4.5	4.2	1.3	3.0	0.5
Rb × 100/K	0.3	0.6	0.4	0.7	0.9	0.7	0.8	0.7	0.7	0.5	0.6	0.6	0.6	*	*

1. Tholeiite (Brunton type), Bingham dyke, Northumberland [HOLMES and HARWOOD

1. (1929), anal., p. 18].

2. Basalt, Cnoc Carnach, Skye [anal., J. H. SCOON].

3. Basalt, non-porphyratic Central type, Monadh Beag, Mull [BAILEY *et al.* (1924),

anal. IV, p. 17].

4. Quartz-dolerite, Garbad silt, Whiting Bay, Arran [TYRRELL (1928), anal. 4, p. 147].

5. Inclinorite pitchstone, N. of Beinn a' Lochain, Mull [BAILEY *et al.* (1924), anal. V,

8. Granophyre, Cnoc Carnach, Skye [anal. J. H. SCOON].

9. Granite (S.55), Skye [anal., J. H. SCOON].

10. Granophyre, Beinn a' Ghraig Ring Dyke, Mull [BAILEY *et al.* (1924), anal. IV, p. 20].11. Rhyolite, Loch Ba Ring Dyke, Mull [BAILEY *et al.* (1924), anal. III, p. 20].

12. Granophyre granite, Central Ring Complex, Arran [TYRRELL (1928), anal. 9, p. 192].

13. Olivine gabbro, Porphyritic Central type [accumulative] Beinn na Duatharach,

14. Basalt, Porphyritic Central type [accumulative] Beinn na Duatharach, Mull

British Tertiary tholeiitic: iron-rich trend

Table 25

	1	2	3	4	5
Si	247.10 ³	240.10 ³	349.10 ³	352.10 ³	218.10 ³
Al	64.10 ³	66.10 ³	58.10 ³	58.10 ³	92.10 ³
Ti	12.10 ³	18.10 ³	2.10 ³	2.10 ³	13.10 ³
Fe ⁺⁺⁺	22.10 ³	30.10 ³	6.10 ³	7.10 ³	20.10 ³
Mg	31.10 ³	24.10 ³	3.10 ³	5.10 ³	30.10 ³
Fe ⁺⁺	82.10 ³	87.10 ³	17.10 ³	17.10 ³	96.10 ³
Na	22.10 ³	23.10 ³	32.10 ³	32.10 ³	24.10 ³
Ca	69.10 ³	65.10 ³	11.10 ³	11.10 ³	69.10 ³
K	8.10 ³	8.10 ³	30.10 ³	30.10 ³	3.10 ³
P	(1300)	(900)	(1300)	(900)	(1300)
Ga	20	20	15	15	25
Cr	30	50	3	*	100
V	200	300	15	5	275
Li	10	15	20	25	10
Ni	15	25	*	*	50
Co	30	35	*	*	30
Sc	35				20
Zr	80	170	250	250	90
Mn	(2000)	(2000)	(3000)	(4000)	(1700)
Y	30	35	50	50	35
Sr	350	300	100	150	400
Pb	*	*	20	20	*
Ba	220	300	1250	1500	150
Rb	40	60	300	300	*
Fe	77	83	88	98	79
Mg	33	17	12	2	21
Fe	63	67	26	28	68
Mg	19	16	3	0.5	17
Alk	18	17	71	71.5	15
Position	-1.0	-0.1	+13.2	+13.5	-2.4

Table 25a

	1	2	3	4	5
Ga × 1000/Al	0.31	0.30	0.26	0.26	0.27
Cr × 1000/Mg	1.0	2.1	1.0	*	3.3
V × 1000/Mg	6.5	12.5	5.0	10.0	9.2
Li × 1000/Mg	0.3	0.6	6.7	50.0	0.3
Ni × 1000/Mg	0.5	1.0	*	*	1.7
Co × 1000/Mg	1.0	1.5	*	*	1.0
Fe/Mg	3.4	4.9	7.7	48.0	3.9
Cr × 1000/Fe	0.3	0.4	0.1	*	0.9
V × 1000/Fe	1.9	2.6	0.7	0.2	2.4
Co × 1000/Fe	0.3	0.3	*	*	0.3
Y × 1000/Ca	0.4	0.5	4.5	4.5	0.5
Sr × 100/Ca	0.5	0.5	0.9	1.4	0.6
Sr × 100/Ca + K	0.5	0.4	0.2	0.4	0.6
Ba × 100/K	2.8	3.8	4.2	5.0	5.0
Rb × 100/K	0.5	0.7	1.0	1.0	*

1. Tholeiite, dyke, N. of Salen, Mull [BAILEY *et al.* (1924), anal. VII, p. 17].
2. Quartz-dolerite, cone sheet, Kilchoan, Ardnamurchan [RICHEY *et al.* (1930), anal. I, p. 82].
3. Pitchstone, dyke, Tormore shore, Arran [TYRRELL (1928), anal. 16, p. 234].
4. Pitchstone, dyke, Glen Shurig, Arran [TYRRELL (1928), anal. 15, p. 234].
5. Olivine gabbro, [accumulative] E. side of Carnas Mor Muck [anal., J. H. SCOON].

British Tertiary tholeiitic: third trend

Table 26

	1	2	3	4	5	6
Si	266.10 ³	274.10 ³	277.10 ³	296.10 ³	317.10 ³	355.10 ³
Al	78.10 ³	71.10 ³	74.10 ³	78.10 ³	65.10 ³	65.10 ³
Ti	5.10 ³	7.10 ³	8.10 ³	6.10 ³	5.10 ³	2.10 ³
Fe ⁺⁺⁺	24.10 ³	22.10 ³	13.10 ³	9.10 ³	22.10 ³	16.10 ³
Mg	31.10 ³	26.10 ³	23.10 ³	17.10 ³	9.10 ³	6.10 ³
Fe ⁺⁺	46.10 ³	52.10 ³	60.10 ³	46.10 ³	25.10 ³	2.10 ³
Na	18.10 ³	20.10 ³	19.10 ³	24.10 ³	22.10 ³	17.10 ³
Ca	59.10 ³	51.10 ³	50.10 ³	36.10 ³	24.10 ³	6.10 ³
K	15.10 ³	18.10 ³	17.10 ³	15.10 ³	34.10 ³	41.10 ³
P	(900)	(830)	(1300)	(900)	(900)	(785)
Ga	15	20	15	25	20	15
Cr	80	80	30	60	20	*
V	150	200	140	70	40	10
Li	25	30	30	15	40	40
Ni	40	25	20	5	5	*
Co	25	25	25	8	5	*
Sc	30	40	20	10	*	*
Zr	100	200	150	150	250	200
Mn	(3000)	(930)	(1500)	(2000)	(2000)	(1500)
Y	35	30	35	20	25	45
Sr	350	300	500	350	350	60
Pb	*	*	*	10	15	30
Ba	600	650	600	1000	1750	2000
Rb	80	100	50	150	250	250
Fe	70	74	76	76	84	97
Mg	30	26	24	24	16	3
Fe	52	53	56	50	42	23
Mg	23	19	17	15	8	1
Alk	25	28	27	35	50	76
Position	+1.4	+3.2	+3.6	+6.1	+10.7	+15.2

Table 26a

	1	2	3	4	5	6
Ga × 1000/Al	0.19	0.28	0.20	0.32	0.31	0.23
Cr × 1000/Mg	2.6	3.1	1.3	3.5	2.2	*
V × 1000/Mg	4.8	7.7	6.1	4.1	4.4	16.7
Li × 1000/Mg	0.8	1.2	1.3	0.9	4.4	66.7
Ni × 1000/Mg	1.3	1.0	0.9	0.3	0.6	*
Co × 1000/Mg	0.8	1.0	1.1	0.5	0.4	*
Fe/Mg	2.3	2.8	3.2	3.2	5.2	30.0
Cr × 1000/Fe	1.1	1.1	0.4	1.1	0.4	*
V × 1000/Fe	2.1	2.7	1.9	1.3	0.9	0.6
Co × 1000/Fe	0.4	0.3	0.3	0.1	0.1	*
Y × 1000/Ca	0.6	0.6	0.7	0.6	1.0	7.5
Sr × 100/Ca	0.6	0.6	1.0	1.0	1.5	1.0
Sr × 100/Ca + K	0.5	0.4	0.7	0.7	0.6	0.1
Ba × 100/K	4.0	3.6	3.5	6.7	5.1	4.9
Rb × 100/K	0.5	0.6	0.3	1.0	0.7	0.6

1. Hypersthene dolerite, composite sill of Bennan, Arran [TYRRELL (1928), anal. 12, p. 204].
2. Cleveland dyke, Bolam, Durham [HOLMES and HARWOOD (1929), anal., p. 39].
3. Cleveland dyke, Great Ayton, Yorkshire [anal., J. H. SCOON].
4. Leidlite pitchstone, Mull [BAILEY *et al.* (1924), anal. III, p. 19].
5. Crainurite, Mull [BAILEY *et al.* (1924), anal. VI, p. 19].
6. Quartz-felspar porphyry, composite sill of Bennan, Arran [TYRRELL (1928), anal. 11, p. 204].

of the function $[(\frac{1}{3} \text{ Si} + \text{ K}) - (\text{ Ca} + \text{ Mg})]$ increases, while Li shows little change. The curves for Cr, Ni, and V decline more rapidly, and the first two are soon practically eliminated. As the initial magma is relatively rich in Fe, its contents of Cr and Ni are low. The rapid decrease of the latter results in the curve for Co lying above that for Ni throughout. Ti decreases steadily, and Sc, present in small amount in the most basic member, soon falls below the limit of sensitivity.

Calcium and Strontium (Fig. 44g). Once again, Ca shows a steady and virtually linear decline as the value of the function $[(\frac{1}{3} \text{ Si} + \text{ K}) - (\text{ Ca} + \text{ Mg})]$ rises, while Sr remains feeble in amount throughout.

Yttrium rises in value to some extent and, with falling Ca in the same direction, the ratio $\text{Y} \times 1000/\text{Ca}$ shows a very marked increase in the acid end-member.

Sodium (Fig. 44g) increases somewhat in the intermediate and later stages, while *Potassium*, *Rubidium*, and *Barium* (Fig. 44g) do the same to a more marked degree. This is especially noticeable in the case of Ba, and less so in the case of Rb.

Lead becomes appreciable in amount only in the acid end-member.

Zirconium, present in appreciable amounts in the basic member, increases steadily, and shows a more than threefold increase in the acid end-member.

(e) *Material for comparison*

As already mentioned, we have for comparison with the above the rocks from Dillsburg, Penn., and those from the Skaergaard intrusion. From the data given by HOTZ (1953) for the former, and by WAGER and MITCHELL (1951) for the latter, the diagrams shown as Figs. 42h, 42i, 43h, 43i, 44h, and 44i have been constructed.

It should be emphasized that both these rock series show a higher degree of absolute enrichment in iron than is shown by any of the series so far dealt with in this paper, and this leads to some interesting differences in behaviour.

Silicon and Oxygen (Figs. 42h, 42i). We have already noted the flat nature of the curves for silicon and oxygen in the earlier stages of some of the tholeiitic series, and this is shown in the Si curve of the Dillsburg series. In the Skaergaard series, however, where the degree of enrichment in Fe was even greater, there is an actual minimum on the Si curve. In both series there is a minimum on the oxygen curve, more marked in that of the Skaergaard series.

Aluminium and Gallium (Figs. 42h, 42i). The curve for aluminium shows a rather sudden drop in the intermediate stages at Dillsburg, and in the Skaergaard series this is represented by a minimum on the curve. Gallium has not been determined for the Dillsburg rocks, but the Ga curve does not show a minimum in the Skaergaard series and, indeed, does not appear to follow Al very closely. The average ratio $\text{Ga} \times 1000/\text{Al}$ here is 0.31.

Magnesium, Nickel, Lithium, Iron, Cobalt, Chromium, Vanadium, and Titanium (Figs. 43h, 43i). Neither of the parental magmas was particularly rich in iron. Consequently they carried appreciable amounts of Cr and had Ni in considerable excess over Co. Both at Dillsburg and at Skaergaard the first two elements are rapidly eliminated, but more rapidly at the latter than at the former. At Skaergaard, Co also falls fairly soon below its limit of sensitivity, but this is not the case at Dillsburg, where enrichment in Fe was less extreme. Mg, again, behaves similarly in both series, but is being eliminated more rapidly at Skaergaard.

Fe shows its maximum enrichment in the Dillsburg rocks at a relatively high value of the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$, and is accompanied by a very marked, and slightly earlier, enrichment in V. At Skaergaard, the enrichment in Fe is considerably greater, takes place at a lower value of the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$, and is again accompanied by an earlier enrichment in V, though this is less marked than in the Dillsburg series. In both cases there is a rapid elimination of V once the maximum has been passed. Li has not been determined for the Dillsburg rocks, but shows no unusual features at Skaergaard. Ti, as would be expected in such iron-enriched trends, passes through a maximum in sympathy with that of Fe, though this is more marked at Dillsburg than at Skaergaard.

Calcium, Strontium, Sodium, Potassium, Rubidium, and Barium (Figs. 44h, 44i). The curves for Ca, Sr, and K are practically identical in the two series and, as usual, Sr remains low throughout. In the Dillsburg rocks, however, the curve for Na rises rather more steeply than that of the Skaergaard series as the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases in value, while Ba remains low. Rb has not been determined for the Dillsburg rocks, but at Skaergaard the Rb curve shows its normal close parallelism with that for K.

Table 27. The Northfield sill

Table 27

	1	2	3	4	5
Si	242.10 ³	281.10 ³	289.10 ³	287.10 ³	354.10 ³
Al	75.10 ³	70.10 ³	73.10 ³	77.10 ³	62.10 ³
Ti	14.10 ³	11.10 ³	11.10 ³	10.10 ³	1.10 ³
Fe'''	13.10 ³	11.10 ³	6.10 ³	6.10 ³	2.10 ³
Mg	35.10 ³	25.10 ³	21.10 ³	17.10 ³	2.10 ³
Fe'	94.10 ³	77.10 ³	67.10 ³	61.10 ³	22.10 ³
Na	19.10 ³	19.10 ³	25.10 ³	30.10 ³	26.10 ³
Ca	56.10 ³	32.10 ³	31.10 ³	24.10 ³	4.10 ³
K	8.10 ³	9.10 ³	16.10 ³	20.10 ³	31.10 ³
P	(1225)	(1965)	(2620)	(2530)	(tr.)
Ga	25	22	20	22	15
Cr	45	*	*	*	*
V	300	100	100	60	*
Li	25	15	15	15	15
Ni	30	*	*	*	*
Co	30	15	15	10	*
Sc	20	*	*	*	*
Zr	150	200	200	300	550
Mn	(2555)	(1705)	(1085)	(1780)	(1160)
Y	25	35	35	35	45
Sr	350	400	300	350	150
Pb	*	*	210	210	20
Ba	350	600	550	600	2200
Rb	25	50	60	60	100
La	*	*	*	*	50
Fe	75	78	78	80	77
Mg	25	22	22	20	23
Fe	63	62	54	50	27
Mg	21	18	16	13	8
Alk	16	20	30	37	65
Position	-0.2	+4.6	+6.0	+7.5	+13.8

Table 27a

	1	2	3	4	5
Ga × 1000/Al	0.33	0.31	0.27	0.29	0.24
Cr × 1000/Mg	1.3	*	*	*	*
V × 1000/Mg	8.6	4.0	4.8	3.5	*
Li × 1000/Mg	0.7	0.6	0.7	0.9	2.1
Ni × 1000/Mg	0.9	*	*	*	*
Co × 1000/Mg	0.9	0.6	0.7	0.6	*
Fe/Mg	3.1	3.5	3.5	3.9	3.4
Cr × 1000/Fe	0.4	*	*	*	*
V × 1000/Fe	2.8	1.1	1.4	0.9	*
Co × 1000/Fe	0.3	0.2	0.2	0.1	*
Y × 1000/Ca	0.4	1.1	1.3	1.5	11.2
Sr × 100/Ca	0.6	1.2	1.0	1.5	3.7
Sr × 100/Ca + K	0.5	1.0	0.6	0.8	0.4
Ba × 100/K	4.4	6.7	3.4	3.0	7.1
Rb × 100/K	0.3	0.6	0.4	0.3	0.3

[Analysis numbers given below are those of Table II (p. 399), in WALKER (1952).]

1. Normal dolerite, zone "b," Northfield Quarry.
2. Coarse grey rock, between zones "c" and "d," Northfield Quarry.
3. Coarse pink rock, zone "c," Northfield Quarry.
4. Medium-grained pink rock, between zones "c" and "d," Northfield Quarry.
5. Pink felsitic vein, zone "c," Northfield Quarry.

(f) *Hawaiian tholeiitic lavas* (Tables 28–30)

The Hawaiian tholeiitic basalts as a whole are characterized by high Ti and low Al, when compared with the other rocks of comparable basicity dealt with in this paper. They also tend to carry more Ni, Zr, and Sr. Otherwise, there is nothing particularly remarkable about them. The lavas of Kilauea (Table 28) are rather

less siliceous and richer in calcium than those of Mauna Loa (Table 29), as has been pointed out by POWERS (1955) and, on the whole, they are somewhat richer in Cr, V, and Ni.

A few results of trace element determinations on these rocks have been given by WAGER and MITCHELL (1953, Table 1, cols. A-E). In general their determinations agree fairly well with ours, except that their values for strontium tend to be higher.

The accumulative rocks at both Kilauea (Table 28, cols. 1-3) and Mauna Loa (Table 29, cols. 1 and 2) are all enriched in dark minerals, especially in olivine. The trace elements show all the expected features, namely, high Cr, Ni, and Co, with less than normal Ga, V, Li, Zr, Sr, and Ba.

The Oahu lavas, belonging to the Koolau series, differ from those of Kilauea and Mauna Loa in being more feldspathic, a feature reflected in their higher content of aluminium. They tend to have slightly higher values for Ga, and are definitely poorer in Cr, V, Li, Co, and Sc (which is below the limit of sensitivity in all the rocks). The examples of accumulative rocks enriched in dark minerals (Table 30,

Table 28. Hawaiian tholeiitic basalts: Kilauea

	1	2	3	4	5	6	7	8
Si	218.10 ³	219.10 ³	221.10 ³	233.10 ³	235.10 ³	231.10 ³	237.10 ³	241.10 ³
Al	41.10 ³	49.10 ³	48.10 ³	66.10 ³	69.10 ³	69.10 ³	74.10 ³	71.10 ³
Ti	11.10 ³	11.10 ³	10.10 ³	15.10 ³	20.10 ³	17.10 ³	22.10 ³	15.10 ³
Fe'''	15.10 ³	11.10 ³	11.10 ³	12.10 ³	8.10 ³	12.10 ³	7.10 ³	9.10 ³
Mg	131.10 ³	121.10 ³	120.10 ³	53.10 ³	44.10 ³	44.10 ³	43.10 ³	46.10 ³
Fe''	82.10 ³	82.10 ³	81.10 ³	79.10 ³	79.10 ³	73.10 ³	76.10 ³	77.10 ³
Na	10.10 ³	12.10 ³	10.10 ³	19.10 ³	17.10 ³	20.10 ³	11.10 ³	15.10 ³
Ca	53.10 ³	55.10 ³	56.10 ³	78.10 ³	81.10 ³	81.10 ³	81.10 ³	77.10 ³
K	2.10 ³	2.10 ³	3.10 ³	5.10 ³	4.10 ³	5.10 ³	4.10 ³	4.10 ³
P	(500)	(650)	(850)	(1750)	(1450)	(5250)	(850)	(1300)
Ga	10	13	15	25	20	22	20	20
Cr	1600	600	1000	500	400	300	300	500
V	200	150	300	300	400	300	400	300
Li	7	10	5	10	10	10	7	10
Ni	1350	750	900	350	350	250	150	300
Co	125	90	70	55	65	45	60	50
Sc	*	?10	20	?10	30	20	30	30
Zr	85	80	120	200	175	150	150	125
Mn	(1400)	(1300)	(1000)	(1100)	(950)	(600)	(1100)	(550)
Y	*	*	25	*	30	20	30	25
Sr	150	150	300	350	450	450	525	450
Pb	*	*	*	*	*	*	*	*
Ba	20	30	70	60	125	125	125	50
Rb	*	*	*	*	*	*	*	*
Fe	43	43	43	63	66	66	66	65
Mg	57	57	57	37	34	34	34	35
Fe	40	41	41	54	57	55	59	57
Mg	55	52	53	32	29	29	30	30
Alk	5	7	6	14	14	16	11	13
Position	-10.9	-10.0	-9.9	-4.8	-4.3	-4.3	-4.1	-3.9

Analysis numbers given below are those in MACDONALD, 1949]

1. Olivine gabbro-porphyr (accumulative) [anal. 2, p. 73].
2. Picrite-basalt (metamorphosed) [accumulative] [anal., J. H. SCOON].
3. Picrite-basalt (1840 flow) [accumulative] [anal. 1, p. 74].

4. Olivine basalt (lava-fountain, 1911) [anal. 6, p. 74].
5. Olivine basalt (1920 flow) [anal. 13, p. 74].
6. Pelee's hair (1920) [anal. 3, p. 74].
7. Olivine basalt (1919 flow) [anal. 12, p. 74].
8. Olivine basalt (prehistoric) [anal. 9, p. 73].

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Table 28a. Hawaiian tholeiitic basalts: Kilauea

	1	2	3	4	5	6	7	8
Ga $\times$ 1000/Al	0.24	0.27	0.31	0.38	0.29	0.32	0.27	0.28
Cr $\times$ 1000/Mg	12.2	5.0	8.3	9.4	9.1	6.8	7.0	10.9
V $\times$ 1000/Mg	1.5	1.2	2.5	5.7	9.1	6.8	9.3	6.5
Li $\times$ 1000/Mg	0.05	0.08	0.04	0.2	0.2	0.2	0.2	0.2
Ni $\times$ 1000/Mg	10.3	6.2	7.5	6.6	8.0	5.7	3.5	6.5
Co $\times$ 1000/Mg	1.0	0.7	0.6	1.0	1.5	1.0	1.4	1.1
Fe/Mg	0.7	0.8	0.8	1.7	2.0	1.9	1.9	1.9
Cr $\times$ 1000/Fe	16.5	6.5	10.9	5.5	4.6	3.5	3.6	5.8
V $\times$ 1000/Fe	2.1	1.6	3.3	3.3	4.6	3.5	4.8	3.5
Co $\times$ 1000/Fe	1.3	1.0	0.8	0.6	0.7	0.5	0.7	0.6
Y $\times$ 1000/Ca	*	*	0.4	*	0.4	0.4	0.4	0.3
Sr $\times$ 100/Ca	0.3	0.3	0.5	0.4	0.6	0.6	0.6	0.6
Sr $\times$ 100/Ca + K	0.3	0.3	0.5	0.4	0.6	0.5	0.6	0.6
Ba $\times$ 100/K	1.0	1.5	2.3	1.2	3.1	2.5	3.1	1.3
Rb $\times$ 100/K	*	*	*	*	*	*	*	*

Table 29. Hawaiian tholeiitic basalts: Mauna Loa

	1	2	3	4	5	6	7
Si	229.10 ³	236.10 ³	241.10 ³	243.10 ³	245.10 ³	243.10 ³	245.10 ³
Al	49.10 ³	66.10 ³	72.10 ³	62.10 ³	58.10 ³	62.10 ³	73.10 ³
Ti	15.10 ³	14.10 ³	12.10 ³	24.10 ³	26.10 ³	29.10 ³	13.10 ³
Fe'''	8.10 ³	13.10 ³	16.10 ³	15.10 ³	13.10 ³	16.10 ³	16.10 ³
Mg	106.10 ³	46.10 ³	48.10 ³	43.10 ³	46.10 ³	44.10 ³	44.10 ³
Fe''	80.10 ³	75.10 ³	71.10 ³	70.10 ³	72.10 ³	69.10 ³	69.10 ³
Na	13.10 ³	13.10 ³	18.10 ³	18.10 ³	17.10 ³	16.10 ³	15.10 ³
Ca	53.10 ³	91.10 ³	74.10 ³	76.10 ³	72.10 ³	71.10 ³	73.10 ³
K	3.10 ³	3.10 ³	3.10 ³	4.10 ³	4.10 ³	3.10 ³	4.10 ³
P	(850)	(2600)	(850)	(1300)	(1300)	(1300)	(1300)
Ga	15	22	30	15	25	20	20
Cr	1750	500	300	300	300	300	300
V	275	275	275	350	250	300	300
Li	5	5	6	10	7	10	7
Ni	2000	700	150	175	200	200	150
Co	150	65	45	60	50	55	50
Sc	20	20	25	20	20	20	25
Zr	100	100	100	125	125	125	150
Mn	(700)	(450)	(950)	(750)	(950)	(850)	(550)
Y	*	20	20	25	30	20	30
Sr	175	350	400	350	350	350	400
Pb	*	*	*	*	*	*	*
Ba	25	50	70	50	100	100	100
Rb	*	*	*	*	*	*	*
Fe	45	66	64	66	65	66	66
Mg	55	34	36	34	35	34	34
Fe	42	59	56	56	56	57	57
Mg	50	31	31	29	30	30	30
Alk	8	10	13	15	14	13	13
Position	—8.0	—5.5	—3.9	—3.4	—3.2	—3.1	—3.1

[Analysis numbers given below are those in MACDONALD, 1949]

1. Pierite-basalt (1868 flow) [accumulative] (anal. 8, p. 63).
2. Olivine basalt (prehistoric) [accumulative] (anal. 5, p. 63).
3. Basalt (1926 flow) (anal. 9, p. 63).

4. Olivine basalt (1919 flow) (anal. 13, p. 63).

5. Basalt (1859 flow) (anal. 12, p. 63).

6. Hypersthene-bearing basalt (1887 flow) (anal. 11, p. 63).

7. Olivine basalt (prehistoric) (anal. 6, p. 63).

Table 29a. Hawaiian tholeiitic basalts: Mauna Loa

	1	2	3	4	5	6	7
Ga $\times$ 1000/Al	0.31	0.33	0.42	0.24	0.43	0.32	0.27
Cr $\times$ 1000/Mg	16.5	10.9	6.3	7.0	6.5	6.8	6.8
V $\times$ 1000/Mg	2.6	6.0	5.7	8.1	5.4	6.8	6.8
Li $\times$ 1000/Mg	0.05	0.1	0.1	0.2	0.2	0.2	0.2
Ni $\times$ 1000/Mg	18.9	15.2	3.1	4.1	4.3	4.5	3.4
Co $\times$ 1000/Mg	1.4	1.4	0.9	1.4	1.1	1.3	1.1
Fe/Mg	0.8	1.9	1.8	2.0	1.9	1.9	1.9
Cr $\times$ 1000/Fe	19.9	5.7	3.4	3.5	3.5	3.5	3.5
V $\times$ 1000/Fe	3.1	3.1	3.2	4.1	2.9	3.5	3.5
Co $\times$ 1000/Fe	1.7	0.7	0.5	0.7	0.6	0.6	0.6
Y $\times$ 1000/Ca	*	0.2	0.3	0.3	0.4	0.3	0.4
Sr $\times$ 100/Ca	0.3	0.4	0.5	0.5	0.5	0.5	0.5
Sr $\times$ 100/Ca + K	0.3	0.4	0.5	0.4	0.5	0.5	0.5
Ba $\times$ 100/K	0.8	1.7	2.3	1.2	2.5	3.3	2.5
Rb $\times$ 100/K	*	*	*	*	*	*	*

Table 30. Hawaiian tholeiitic basalts: Oahu (Koolau series)

	1	2	3	4	5	6	7	8	9
Si	235.10 ³	240.10 ³	231.10 ³	237.10 ³	245.10 ³	246.10 ³	246.10 ³	254.10 ³	226.10 ³
Al	68.10 ³	73.10 ³	86.10 ³	85.10 ³	79.10 ³	76.10 ³	79.10 ³	75.10 ³	95.10 ³
Ti	9.10 ³	13.10 ³	14.10 ³	13.10 ³	15.10 ³	16.10 ³	10.10 ³	11.10 ³	22.10 ³
Fe'''	22.10 ³	17.10 ³	29.10 ³	26.10 ³	24.10 ³	20.10 ³	22.10 ³	22.10 ³	36.10 ³
Mg	85.10 ³	62.10 ³	43.10 ³	41.10 ³	40.10 ³	44.10 ³	41.10 ³	41.10 ³	25.10 ³
Fe''	60.10 ³	60.10 ³	57.10 ³	61.10 ³	53.10 ³	64.10 ³	58.10 ³	57.10 ³	51.10 ³
Na	18.10 ³	19.10 ³	21.10 ³	18.10 ³	19.10 ³	19.10 ³	28.10 ³	22.10 ³	30.10 ³
Ca	54.10 ³	61.10 ³	72.10 ³	71.10 ³	71.10 ³	67.10 ³	58.10 ³	59.10 ³	63.10 ³
K	1.10 ³	5.10 ³	2.10 ³	2.10 ³	2.10 ³	3.10 ³	5.10 ³	4.10 ³	7.10 ³
P	(175)	(1225)	(350)	(525)	(1530)	(1530)	(2880)	(1200)	(1570)
Ga	20	20	30	25	25	25	30	25	25
Cr	1250	400	225	250	225	225	250	200	25
V	175	175	150	150	275	150	200	120	225
Li	5	5	5	5	7	5	7	7	10
Ni	700	250	75	75	85	75	80	80	70
Co	75	55	30	35	30	30	50	50	30
Sc	—	—	*	*	*	*	*	*	*
Zr	100	125	100	100	150	100	150	100	175
Mn	(695)	(850)	(465)	(850)	(775)	(620)	(385)	(1100)	(465)
Y	15	15	15	20	20	15	25	*	25
Sr	350	375	350	400	350	350	350	400	1000
Pb	*	*	*	*	*	*	*	*	*
Ba	50	150	65	100	75	100	100	75	150
Rb	*	5	*	*	*	5	5	*	5
Fe	49	55	67	68	66	66	66	66	78
Mg	51	45	33	32	34	34	34	34	22
Fe	44	47	57	58	56	56	52	54	58
Mg	46	38	28	28	29	29	27	28	17
Alk	10	15	15	14	15	15	21	18	25
Position	-6.0	-3.8	-3.7	-3.1	-2.7	-2.6	-1.2	-1.1	-0.6

[Analysis numbers given below are those in WENTWORTH and WINCHELL, 1947]

1. Melabasalt porphyry [accumulative] (anal. 9, p. 71).
2. Hypersthene-bearing melabasalt porphyry [accumulative] (anal. 4, p. 71).
3. Basalt porphyry (anal. 10, p. 71).
4. Melabasalt (anal. 7, p. 71).
5. Altered melabasalt (anal. 3, p. 71).
6. Melabasalt (anal. 2, p. 71).
7. Intrusive dolerite (anal. 1, p. 71).
8. Hypersthene basalt, dyke (anal., J. H. Scoon).
9. Plagioclase basalt porphyry [accumulative] (anal. 11, p. 71).

Table 30a. Hawaiian tholeiitic basalts: Oahu

	1	2	3	4	5	6	7	8	9
Ga $\times$ 1000/Al	0.29	0.27	0.35	0.29	0.32	0.33	0.38	0.33	0.26
Cr $\times$ 1000/Mg	14.9	6.5	5.2	6.1	5.6	5.1	6.1	4.9	1.0
V $\times$ 1000/Mg	2.1	2.8	3.5	3.7	6.9	3.4	4.9	2.9	9.0
Li $\times$ 1000/Mg	0.06	0.08	0.1	0.1	0.2	0.1	0.2	0.2	0.4
Ni $\times$ 1000/Mg	8.2	4.0	1.7	1.8	2.1	1.7	2.0	2.0	2.8
Co $\times$ 1000/Mg	0.9	0.9	0.7	0.9	0.8	0.7	1.2	1.2	1.2
Fe/Mg	1.0	1.2	2.0	2.1	1.9	1.9	2.0	1.9	3.5
Cr $\times$ 1000/Fe	15.2	5.2	2.6	2.9	2.9	2.7	3.1	2.5	0.3
V $\times$ 1000/Fe	2.1	2.3	1.7	1.7	3.6	1.8	2.5	1.5	2.6
Co $\times$ 1000/Fe	0.9	0.7	0.3	0.4	0.4	0.4	0.6	0.6	0.3
Y $\times$ 100/Ca	0.3	0.2	0.2	0.3	0.3	0.2	0.4	*	0.4
Sr $\times$ 100/Ca	0.6	0.6	0.5	0.6	0.5	0.5	0.6	0.7	1.6
Sr $\times$ 100/Ca + K	0.6	0.6	0.5	0.5	0.5	0.5	0.6	0.6	1.4
Ba $\times$ 100/K	5.0	3.0	3.2	5.0	3.8	3.3	2.0	1.9	2.1
Rb $\times$ 100/K	*	0.1	*	*	*	0.2	0.1	*	0.1

cols. 1 and 2) show the usual features, while that enriched in plagioclase feldspar (Table 30, col. 9) shows a corresponding enrichment in Al and Sr, with decrease, especially, in Cr.

If these lavas have all been derived from a common parental magma (but see POWERS, 1955), the latter is presumably represented by the most basic normal type found at Kilauea (Table 28, col. 4).

(g) *The Satakunta dolerite-granite hybrids (Table 31 and Figs. 45a, 45b, 45c).*

These hybrids, formed from an iron-rich tholeiitic magma which has assimilated varying amounts of rapakivi granite, are of interest to compare with the tholeiitic series already considered, whose variation is believed to be due, at least very largely, to processes of magmatic differentiation.

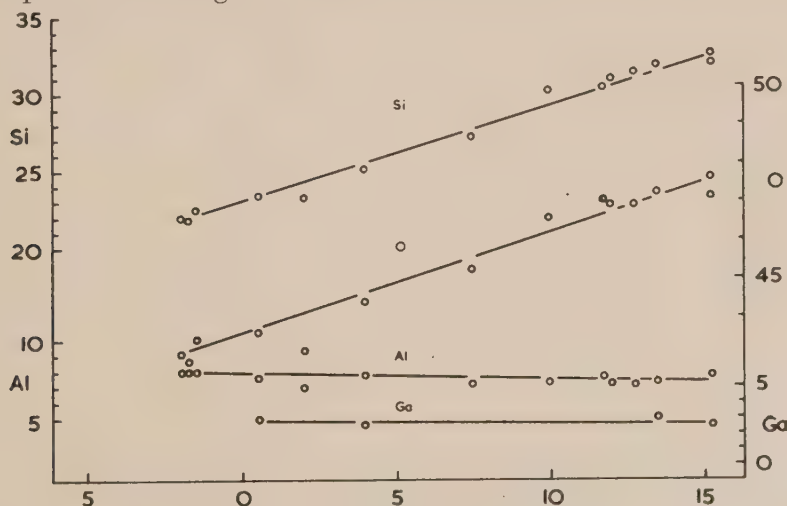


Fig. 45a. Variation in silicon, oxygen, aluminium, and gallium in the Satakunta hybrids. Values in weight per cent with Ga $\times$ 1000.

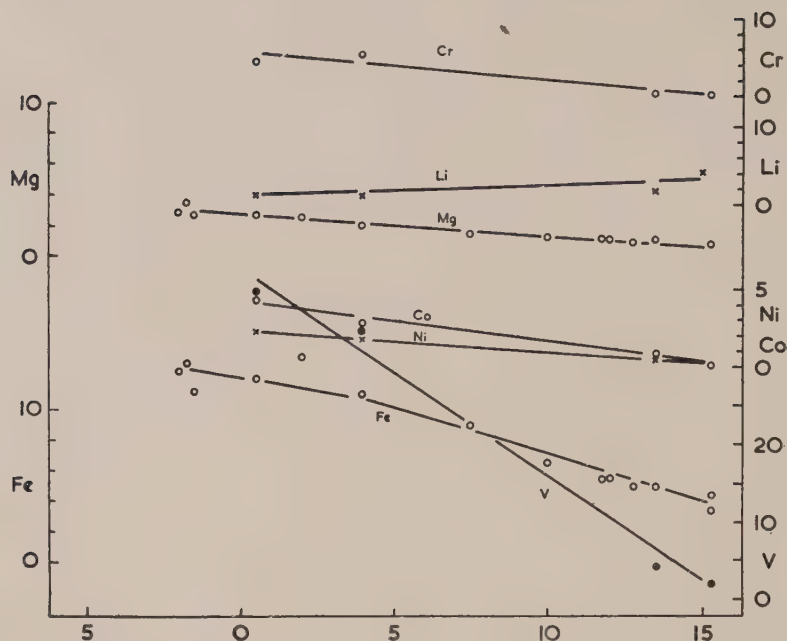


Fig. 45b. Variation in chromium, lithium, magnesium, nickel, cobalt, iron, and vanadium in the Satakunta hybrids. Values in weight per cent with Cr, Li, Ni, Co, and V $\times 1000$.

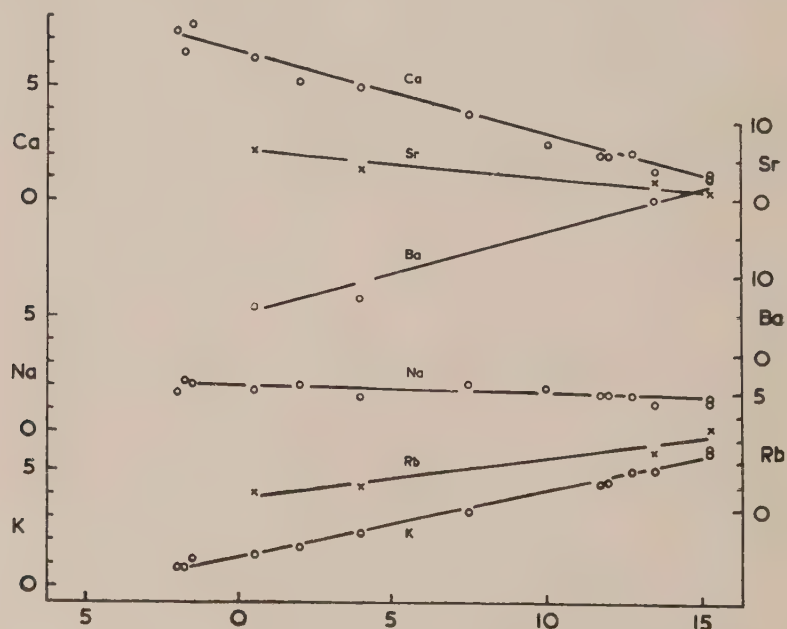


Fig. 45c. Variation in calcium, strontium, barium, sodium, rubidium, and potassium in the Satakunta hybrids. Values in weight per cent with Sr, Ba, and Rb $\times 100$.

Table 31. Dolerite-granite hybrids, etc., Satakunta, Finland

	1	2	3	4	5	6	7	8	9
Si		234.10 ³	251.10 ³		318.10 ³	325.10 ³	331.10 ³	344.10 ³	349.10 ³
Al		77.10 ³	78.10 ³		73.10 ³	78.10 ³	61.10 ³	66.10 ³	60.10 ³
Ti		13.10 ³	11.10 ³		4.10 ³	3.10 ³	4.10 ³	2.10 ³	1.10 ³
Fe ^{'''}		19.10 ³	16.10 ³		10.10 ³	15.10 ³	7.10 ³	11.10 ³	13.10 ³
Mg		27.10 ³	19.10 ³		8.10 ³	3.10 ³	8.10 ³	1.10 ³	8.10 ³
Fe ^{''}		99.10 ³	92.10 ³		38.10 ³	17.10 ³	32.10 ³	13.10 ³	11.10 ³
Na		18.10 ³	15.10 ³		13.10 ³	13.10 ³	18.10 ³	15.10 ³	19.10 ³
Ca		61.10 ³	49.10 ³		13.10 ³	11.10 ³	21.10 ³	7.10 ³	4.10 ³
K		14.10 ³	23.10 ³		50.10 ³	58.10 ³	42.10 ³	60.10 ³	48.10 ³
P	—	(1310)	(1266)	—	(525)	(480)	(435)	—	—
Ga	25	30	25	30	30	25	15	20	25
Cr	65	45	60	*	3	1	*	*	*
V	300	350	300	250	40	10	*	*	*
Li	20	20	15	15	20	45	10	35	100
Ni	100	25	20	8	5	5	3	*	*
Co	60	45	30	20	8	*	*	*	*
Sc	20	20	20	*	*	*	*	*	*
Zr	150	200	200	400	450	700	150	275	80
Mn	—	(1625)	(1395)	—	(620)	(310)	(385)	(230)	(310)
Y	35	35	35	60	80	140	70	70	140
Sr	450	650	400	300	250	100	25	25	20
Pb	*	*	*	*	30	20	40	25	25
Ba	350	650	700	1000	2000	2250	3000	500	650
Rb	*	75	90	125	250	350	150	500	300
La	55	80	40	40	140	100	45	70	70
Mo	*	*	*	3	3	2	2	?2	*
Be	*	*	*	*	5	7	*	5	10
Fe	—	81	85	—	86	91	83	96	75
Mg	—	19	15	—	14	9	17	4	25
Fe	—	67	65	—	40	30	36	24	24
Mg	—	15	12	—	7	3	7	1	8
Alk	—	18	23	—	53	67	57	75	68
Position	—	+0.4	+3.9	—	+13.5	+15.2	+12.3	+16.7	+15.2

1. Fine-grained dolerite.

2. Dolerite hybrid (KAHMA, 1951, anal. 2, p. 46).

3. Dolerite hybrid (KAHMA, 1951, anal. 3, p. 46).

4. Dolerite hybrid.

5. Rapakivi hybrid (KAHMA, 1951, anal. 5, p. 46).

6. Normal rapakivi granite (KAHMA, 1951, anal. 13, p. 46).

7. Palingenic dyke from normal rapakivi granite, cutting fine-grained dolerite (No. 1) (KAHMA, 1951, anal. 6, p. 32).

8. Spotted granite (KAHMA, 1951, anal. 9, p. 32).

9. Palingenic dyke from spotted granite (KAHMA, 1951, anal. 5, p. 32).

Table 31a. Hybrids, etc., Satakunta, Finland

	2	3	5	6	7	8	9
Ga × 1000/Al	0.39	0.32	0.41	0.32	0.25	0.30	0.42
Cr × 1000/Mg	1.7	3.2	0.4	0.3	*	*	*
V × 1000/Mg	13.0	15.8	5.0	3.3	*	*	*
Li × 1000/Mg	0.7	0.8	2.5	15.0	1.3	35.0	12.5
Ni × 1000/Mg	0.9	1.1	0.6	1.7	0.4	*	*
Co × 1000/Mg	1.7	1.6	1.0	*	*	*	*
Fe/Mg	4.4	5.7	6.0	10.7	4.9	24.0	3.0
Cr × 1000/Fe	0.4	0.6	0.1	0.03	*	*	*
V × 1000/Fe	3.0	2.8	0.8	0.3	*	*	*
Co × 1000/Fe	0.4	0.3	0.2	*	*	*	*
Y × 1000/Ca	0.6	0.7	6.1	12.7	0.3	10.0	35.0
Sr × 100/Ca	1.1	0.8	1.9	0.9	0.1	0.4	0.5
Sr × 100/Ca + K	0.9	0.6	0.4	0.2	0.04	0.04	0.04
Ba × 100/K	4.6	3.0	4.0	3.9	7.1	0.8	1.4
Rb × 100/K	0.5	0.4	0.5	0.6	0.4	0.8	0.6

The most striking feature is the linear variation of all the major elements when these are plotted against the function $[(\frac{1}{3} \text{ Si} + \text{K}) - (\text{Ca} + \text{Mg})]$. We had, unfortunately, only four of the analysed rocks on which to make trace element determinations. But the results of these, at least, are not inconsistent with the view that the variation of the trace elements is linear as well.

It would be interesting to know if such linear variation is to be regarded as typical of hybrid series of this kind, or whether it is fortuitous.

Table 32. Approximate chemical composition of some tholeiitic parental magmas

	1	2	3	4	5	6
Si	233.10 ³	237.10 ³	245.10 ³	240.10 ³	238.10 ³	242.10 ³
Al	66.10 ³	88.10 ³	79.10 ³	79.10 ³	79.10 ³	75.10 ³
Ti	15.10 ³	5.10 ³	7.10 ³	7.10 ³	5.10 ³	14.10 ³
Fe'''	12.10 ³	4.10 ³	12.10 ³	13.10 ³	15.10 ³	13.10 ³
Mg	53.10 ³	44.10 ³	44.10 ³	42.10 ³	44.10 ³	35.10 ³
Fe''	79.10 ³	75.10 ³	69.10 ³	66.10 ³	78.10 ³	94.10 ³
Na	19.10 ³	12.10 ³	14.10 ³	15.10 ³	9.10 ³	19.10 ³
Ca	78.10 ³	89.10 ³	76.10 ³	84.10 ³	84.10 ³	56.10 ³
K	5.10 ³	1.10 ³	5.10 ³	7.10 ³	2.10 ³	8.10 ³
Ga	25	30	—	20	25	25
Cr	500	425	200	250	63	45
V	300	220	250	275	475	300
Li	10	5	—	20	6	25
Ni	350	150	38	60	18	30
Co	55	50	35	55	42	30
Sc	110	20	—	40	57	20
Zr	200	65	58	80	42	150
Y	*	20	22	20	10	25
Sr	350	125	400	200	178	350
Pb	*	*	—	*	*	*
Ba	60	70	125	170	80	350
Rb	*	*	—	20	*	25
Fe	63	64	65	65	68	75
Mg	37	36	35	35	32	25

1. Hawaiian tholeiitic basalts [Table 28, col. 4].

2. Karoo dolerites [Table 22, col. 4].

3. Dillsburg sill [average of two, Hotz (1953)].

4. British Tertiary tholeiitic [Table 24, col. 1].

5. Hakone volcanic rocks [average of two, Table 18, cols. 9 and 10].

6. Northfield sill [Table 27, col. 1].

Palingenic dykes. Associated with these hybrids there are various palingenic dykes derived from granite and sandstone. Trace element determinations for two of these, both derived from granite, are given in Table 31 (cols. 7 and 9), together with the granites from which they are derived (Table 31, cols. 6 and 8).

A noticeable feature of both these palingenic dykes is their comparative richness in magnesium, recalling in this respect the metasomatic granophyres associated with the Karroo dolerites. The first example (Table 31, col. 7) is richer in Si, Ca, and Na, and poorer in Al and K than the parent rock (Table 31, col. 6). It is poorer in all the trace elements except Ba and Pb. The second example (Table 31, col. 9) is richer in Si and Na, and poorer in Al, Ca, and K, than the parent rock (Table 31, col. 8). It is poorer in Zr and Rb, but richer in Li, Y, and Be.

It is particularly interesting to notice the low values of Zr in both these

palingenic dykes, when compared with their parent rocks. This is what we might expect in view of the refractory nature of zircon.

Caesium and *tin* have not been found above their limits of sensitivity in any of the rocks investigated for this paper. The same applies to *molybdenum* and *lanthanum*, with the exception of the rock represented by Table 22, col. 9, and the hybrids just dealt with (Table 31).

THE PARENTAL MAGMAS

The assumed parental magmas for the various series are brought together in Table 32. There is, on the whole, a good correlation between the amounts of Cr, Ni, and, to a less extent, Co present and the Fe/Mg ratio. But they cannot all be considered as belonging to a single trend, because Na and K, in particular, do not vary consistently. Neither do Li, Sr, or Ba, which tend to vary in sympathy with either K or Na. Zirconium, again, is rather variable.

The possible relations between these, and other, parental magmas of tholeiitic type, and between those and parental magmas of alkali and calc-alkali type, will be the subject of our fourth paper.

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Gallium in chondrites

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ABSTRACT

Chondrites have uniform gallium contents; the average of nineteen samples is 5.3 p.p.m. Ga, with the range 4.2–6.8 p.p.m. Composites of these contain an average of 3.2 p.p.m. Ga in the silicate phase, 15 p.p.m. in the metal phase, and 12 p.p.m. in the sulphide phase. The chalcophilic character of gallium is approximately as strong as the siderophilic on the basis of these figures. The gallium content of the silicate phase of chondrites is much the same as of ultramafic rocks, and the ratios Ga/Al are similar for the two.

ACCORDING to present views, the abundance of non-volatile elements in chondrites should correspond quite well to the cosmic abundance of such elements. Determination of gallium in silicate meteorites has not been undertaken since the work of GOLDSCHMIDT and the NODDACKS more than twenty years ago. Analytical methods now available for the determination of gallium are more sensitive and precise than those used by the early workers, and it seemed worthwhile to re-investigate the gallium content of chondrites.

Table 1. Summary of previous data and estimates of gallium in meteorites

	Ga, p.p.m.	Author
Iron meteorites, average	13	NODDACKS (1930)
Iron meteorites, average	5	GOLDSCHMIDT and PETERS (1931)
Silicate of siderolite, Estherville, Iowa	5	GOLDSCHMIDT and PETERS (1931)
Iron of siderolite, Estherville, Iowa	<5	GOLDSCHMIDT and PETERS (1931)
Chondrite, Homestead, Iowa	<5	GOLDSCHMIDT and PETERS (1931)
Chondrite, Long Island, Kansas	<5	GOLDSCHMIDT and PETERS (1931)
Carbonaceous chondrite, Orgueil, France	5	GOLDSCHMIDT and PETERS (1931)
Olivine of pallasite, Brenham, Kansas	not detected	GOLDSCHMIDT and PETERS (1931)
Iron of pallasite, Brenham, Kansas	5	GOLDSCHMIDT and PETERS (1931)
Chondrites, average	4.6	NODDACKS (1934)
Silicate phase of meteorites, average	3	GOLDSCHMIDT (1937)
Nickel iron meteorites, average	8	GOLDSCHMIDT (1937)
Troilite, average	8	GOLDSCHMIDT (1937)
Meteorites (10 parts silicate, 2 parts iron, and 1 part troilite), average	4.2	GOLDSCHMIDT (1937)
45 iron meteorites	0.43–96.3; average 35.7	GOLDBERG, UCHIYAMA, and BROWN (1951)
Troilite of Canyon Diablo iron	0.4	GOLDBERG <i>et al.</i> (1951)
Troilite of Xiquipileo iron	0.3	GOLDBERG <i>et al.</i> (1951)
Metal phase of pallasite, Admire, Kansas	21.4	GOLDBERG <i>et al.</i> (1951)
Metal phase of pallasite, Springwater, Canada	17.9	GOLDBERG <i>et al.</i> (1951)

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Table 1 summarizes most of the previous data on gallium in meteorites, both silicate and iron. The sensitivity of GOLDSCHMIDT and PETERS'S (1931) spectrographic method was only about 5 p.p.m. Ga_2O_3 (4 p.p.m. Ga), so that their values are highly approximate. The results of GOLDBERG *et al.* (1951) were obtained by a neutron activation method, the error of which is stated to be 10 per cent.

ANALYTICAL METHOD

A photometric method was used in which gallium is determined as rhodamine B chlorogallate (extracted by benzene) after isolation of gallium by isopropyl ether extraction of chlorogallic acid (ONISHI and SANDELL, 1955).

Chondrites (0.5 g powder) were first treated with aqua regia to dissolve the metal and troilite. Following evaporation to fumes with sulphuric acid, the residue was treated with hydrofluoric acid to bring silicates into solution. The excess of hydrofluoric and sulphuric acids was expelled and the residue was taken up in 7 *M* hydrochloric acid. Gallium was then extracted with isopropyl ether and determined photometrically with rhodamine B, as described in the reference cited. A Leitz-Rouy photometer with a 550 $\text{m}\mu$ filter was used for measurement of absorbance. The error is believed to lie within ± 10 per cent.

The metal and silicate phases of chondrites were separated magnetically. Some silicate accompanies the metal, and its amount was found by igniting and weighing the residue remaining after treatment of the magnetic fraction with aqua regia. Some silicate is decomposed and brought into solution by the acid treatment. To correct for this, the weight of the residue was multiplied by 1.5 to give the weight of silicate. This factor was determined experimentally by treating the silicate fraction with acid in the same way. The magnetic fractions contained about 35 per cent silicate. Some gallium will be introduced from the decomposed silicate. If all the silicate is decomposed, the apparent value for gallium in the iron phase will be increased about 10 per cent. However, all the silicate may not be decomposed and therefore a correction has not been applied. A few per cent of troilite was also present in the magnetic fraction, but since the gallium contents of metal and troilite are much the same, no correction was applied for this.

Troilite in the non-magnetic fraction was brought into solution by leaching for ten minutes at room temperature with 0.1 *M* hydrochloric acid saturated with bromine. The solution thus obtained was analysed for gallium. Another portion of the non-magnetic fraction was analysed for sulphur after treatment with bromine in carbon tetrachloride, followed by nitric acid. In this way the ratio Ga : S was found, and therefore Ga : FeS. The suitability of this solution method was checked by the use of a finely powdered sample of terrestrial troilite (Del Norte Co., Calif.). The hydrochloric acid-bromine leach gave 60.2 per cent Fe or 94.8 per cent FeS, and the carbon tetrachloride-bromine-nitric acid solution gave 33.9 per cent S or 93.0 per cent FeS. A slight residue of silica or silicate remained after the acid treatment. These results are taken to mean that satisfactorily complete solution of troilite is obtained by the hydrochloric acid-bromine leaching; presumably gallium will be brought into solution if iron is. Doubtless some attack of silicate by dilute hydrochloric acid occurs, but the amount of gallium thus introduced should not exceed 1 p.p.m. referred to troilite.

The residue from the treatment of the non-magnetic fraction with 0.1 *M* hydrochloric acid-bromine was analysed for gallium after decomposition with hydrofluoric-sulphuric acid.

RESULTS AND DISCUSSION

Table 2 gives the gallium content of individual chondrite samples, and Table 3 the gallium content of the silicate, metal, and sulphide phases of chondrites. The frequency distribution is shown in Fig. 1. All the determinations were made by ONISHI.

Table 2. Gallium in chondrites

	Description*	Ga, p.p.m.
Alamogordo, N. Mex.	Crystalline spherical chondrite	4.8
Arriba, Colo.	Polymict brecciated intermediate chondrite	6.0
Beenham, N. Mex.	Veined grey hypersthene chondrite (LEARD) or intermediate chondrite (WAHL)	5.6
Cope, Colo.		4.2
Cotesfield, Nebr.		4.7
Estacado, Texas	Crystalline bronzite chondrite	6.4
Gladstone, N. Mex.	Black veined crystalline spherical chondrite	6.8
Gruver, Texas		4.6
Haven, Kan.		5.6
Hesston, Kan.		4.6
Kingfisher, Okla.	Black chondrite	5.1
Ladder Creek, Kan.	Crystalline spherical chondrite	5.6
Melrose, N. Mex.	Hypersthene chondrite	5.2
Miller, Kan.		6.0
Morland, Kan.	Crystalline chondrite	5.1
Plainview, Texas	Polymict brecciated veined intermediate chondrite	5.4
Potter, Nebr.	Polymict brecciated grey chondrite, with large portions of black chondrite	4.8
Roy, N. Mex.	Crystalline spherical bronzite chondrite	5.5
Tryon, Nebr.	Grey chondrite	4.4
	Average	5.3

* PRIOR and HEY (1953)

The average for nineteen chondrites is 5.3 p.p.m. Ga, with a range from 4.2 to 6.8 p.p.m. The silicate phase of chondrites contains 3.2 p.p.m. Ga as an average based on analysis of composites. This value agrees with GOLDSCHMIDT's rough estimate of 3 p.p.m. for the silicate phase of meteorites. The average of the metal phase of chondrites is 15 p.p.m. Ga. This value is less than one-half the average for iron meteorites (GOLDBERG *et al.*, 1951). Although only a few individual values for gallium in the metal phase of chondrites were obtained, it appears likely that the metal phase is much more uniform in gallium content than are iron meteorites. Our value of 12 p.p.m. Ga for troilite of chondrites is comparable with GOLDSCHMIDT's estimate of 8 p.p.m. It is much greater than the value reported for two troilites of iron meteorites by GOLDBERG *et al.*

Table 3. Gallium in component phases of chondrites

	Percentage of chondrite	Ga, p.p.m.
Composite I (Arriba, Beenham, Cope, Cotesfield, Morland, Plainview, Roy)		5.2*
Silicate phase	84	3.2
Metal phase	11	12, 14
Sulphide phase	5	10
Composite II (Alamogordo, Estacado, Gladstone, Gruver, Kingfisher, Ladder Creek, Melrose)		5.5†
Silicate phase	82	3.2
Metal phase	13	17, 18
Sulphide phase	5	14
Composite III (Beenham, Estacado, Kingfisher, Potter)		5.5
Silicate phase		3.0
Sulphide phase		9
Metal phase, Cotesfield	5	18
Metal phase, Estacado	16	16
Metal phase, Haven	15	17

* From individual values of Table 2. By summation of gallium contents of silicate, metal, and sulphide phases the value 4.6 p.p.m. is obtained.

† From individual values of Table 2. By summation of gallium contents of silicate, metal, and sulphide phases the value 5.6 is obtained.

Because some of the chondrites used in the present work are considerably weathered and limonitized, it is necessary to consider whether this alteration has affected the original gallium content. We believe that no important change in gallium content has occurred, inasmuch as there is no apparent relationship between

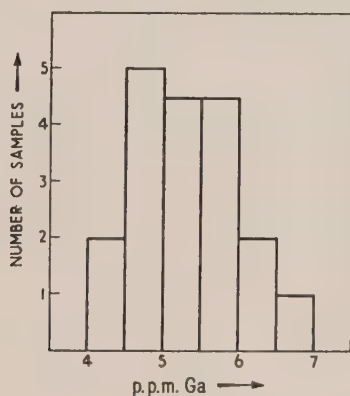


Fig. 1. Frequency diagram of gallium in nineteen chondrites

the gallium content and the degree of weathering of the chondrites examined. Thus, for example, the Estacado chondrite, which is the freshest in our collection, contains 6.4 p.p.m. Ga, as compared to 6.0 p.p.m. in the weathered Miller chondrite. Composite III consists of the four freshest of the nineteen chondrites; its average of

5.5 p.p.m. is practically the same as the average of 5.3 p.p.m. for all nineteen chondrites. The silicate phase of Composite III contains 3.0 p.p.m., which agrees with 3.2 p.p.m. for nineteen samples.

The present data make gallium more siderophilic than the earlier data, i.e., $[\text{Ga}]_{\text{metal}}/[\text{Ga}]_{\text{silicate}} = 15/3.2 = \sim 5$, as compared to the Goldschmidt ratio $8/3 = \sim 3$. They also show that the chalcophilic character of gallium, as expressed by the ratio $[\text{Ga}]_{\text{sulphide}}/[\text{Ga}]_{\text{silicate}} = 12/3.2 = \sim 4$, is almost as marked as the siderophilic character. The gallium content of the silicate phase of chondrites is comparable to that of ultramafic rocks, for which GOLDSCHMIDT and PETERS (1931) reported $\ll 4$ p.p.m. Ga, and SANDELL (1949) reported about 2 p.p.m. Ga. UREY and CRAIG (1953) calculated an average of 3.09 per cent Al_2O_3 or 1.62 per cent Al for the silicate phase of ninety-four chondrites. Assuming that the aluminium content of the silicate phase of the chondrites used is the same as this, the weight ratio $\text{Ga}/\text{Al} = 3.2/1.6 \times 10^4 = 2.0 \times 10^{-4}$ for the silicate phase of chondrites is obtained. This value is similar to the ratio of $(1.5 \pm) \times 10^{-4}$ for ultramafic rocks obtained by SANDELL (1949). Gallium in the silicate phase makes up about 50 per cent of the total gallium content of chondrites.

If we adopt the Urey-Craig average for silicon in chondrites, namely 18 per cent Si, we obtain the weight ratio $\text{Ga}/\text{Si} = 5.3/18 \times 10^4 = 3 \times 10^{-5}$, or the atomic ratio 1.2×10^{-5} . For the silicate phase of chondrites the weight ratio Ga/Fe is $3.2/1.2 \times 10^5 = 2.7 \times 10^{-5}$. For the metal phase of chondrites the same ratio is $15/9 \times 10^5 = 1.7 \times 10^{-5}$.

Gallium (atomic number 31) is less abundant than zinc (A.N. 30) and germanium (A.N. 32), if the respective contents are taken as 80 and 55 p.p.m. in chondrites.

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Frequency-distributions of elements in igneous rocks

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ABSTRACT

A proposed geochemical law which states that "the concentration of an element in a specific igneous rock is lognormally distributed" is critically reviewed. It is shown (a) that a lognormal law cannot apply even approximately to all the major constituents of a rock, and (b) that many minor elements will follow major constituents in failing to obey such a law. It is demonstrated that the dispersions of AHRENS's data for the minor elements of granite and diabase, and the extents which they exhibit an approximate lognormality, conform very largely with the known associations of the elements with other constituents of the two rock-types.

INTRODUCTION

AHRENS (1953, 1954a, b) has recently published three papers dealing with a proposed new law of geochemistry. The law states that "the concentration of an element is lognormally distributed in a specific igneous rock."

The present author (AUBREY, 1954) has already commented on the first of these papers, which contained only a limited number of supporting data (AHRENS, 1953). AHRENS's second, and main, contribution (1954) has been criticized by CHAYES (1954), chiefly on the grounds that the data presented are likely to be insufficient to establish the law. Some of the points already touched on by the present author are additional to those made by CHAYES, and have been given added weight by the appearance of the main body of AHRENS's supporting data.

MAIN POINTS OF CRITICISM OF THE PROPOSED LAW

Without going into the question of whether the majority of AHRENS's examples do in fact mathematically conform best to a lognormal distribution, it is contended that the law, as stated, is invalid, firstly because it is impossible for all the major constituent elements of a material to exhibit lognormal distributions, and secondly because there must be many examples of minor constituents which will follow a particular major constituent in its departure from a lognormal distribution.

Neither type of departure from a lognormal distribution will be a rare event. The first type will be encountered in the analytical data for any material: the second type is apparently not uncommon, and is exemplified by some of the data already published by AHRENS.

MAIN CONSTITUENTS OF AN IGNEOUS ROCK

It might be contended that the first point of criticism is without substance, since all the examples which AHRENS has quoted are of minor constituents, and the law was therefore intended to apply only to such constituents. The law as stated, however, is quite unequivocal in its meaning. If some limitation in the connotation of "an element" were intended, it would presumably have been specified.

In the simple case of a material with only two main constituents, it is clear that,

if the distribution of concentration of one of these is positively skewed, or approximately lognormal, then that of the other constituent must be negatively skewed, a mirror-image of the first distribution. This is illustrated in Fig. 1, where curve *A* represents the plotting of a lognormal distribution on a linear basis. The distribution of values for the other constituent would then be represented by curve *B*, and it is clear that it departs very much from a lognormal type.

When the number of main constituents is greater than two, the position is not so clear-cut, but it is suggested that at least one of the constituents will show a

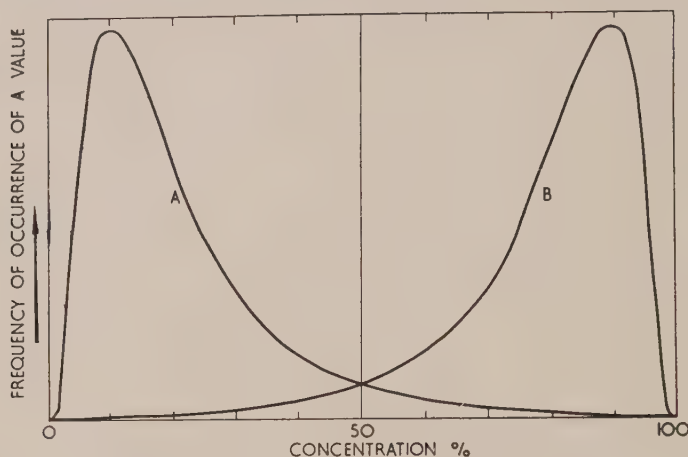


Fig. 1. Distributions of concentration-values in a two-component system.
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certain amount of negative skewness in its distribution. This may be shown by considering first a three-component mixture of constituents *A*, *B*, and *C*, and assuming that two of these components, *A* and *B*, Fig. 2, have lognormal, or positively skewed, distributions. If the values of *A* and *B* are paired off at random and added, then a series of values for a combined constituent, (*A* + *B*), will be obtained. A graphical treatment on these lines will indicate that the frequency distribution for the combined constituents (*A* + *B*), Fig. 2, retains some of the positive skewness of the distribution of the individual constituents. Applying then the argument outlined in the last paragraph, it is apparent that the third constituent, *C*, must have a certain amount of negative skewness in its distribution. The argument may be extended to systems containing more than three constituents, again assuming that all but one of the constituents have values which are lognormally distributed. The random summation of these lognormally distributed constituents will then give a distribution which retains a certain amount of positive skewness. The distribution of concentration-values for the last constituent will be a mirror image of this and will therefore exhibit a certain amount of negative skewness. It will therefore differ from the lognormal.

This treatment also suggests that as long as one is dealing with *independent* constituents of a material, the less abundant constituents will tend to have values with positively skewed distributions and the more abundant constituents to have

dispersions exhibiting increased amounts of negative skewness. It is probably permissible to consider this as due to differences between the ways in which the two types of data, high and low, can be distributed between 0 and 100 per cent. High levels of concentration (over 50 per cent) have more opportunities of varying to low values than to high, and therefore the dispersion in the data will tend to be negatively skewed. The reverse would apply to low levels of concentration, and these might consequently be expected to be positively skewed, or approximately lognormal, in their distribution.

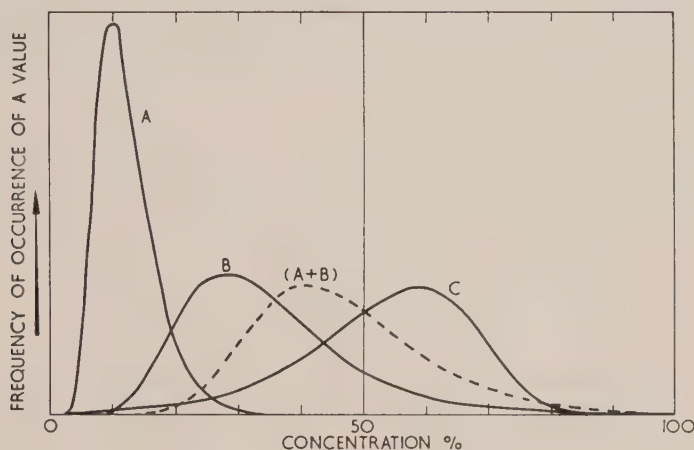


Fig. 2. Distributions of concentration-values in a three-component system.
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The fact that the law as propounded by AHRENS is limited to specific igneous rocks will naturally limit the range of variation of the main constituents. This should not affect the above argument; it is in fact likely to decrease the possibility of any of the main constituents exhibiting truly lognormal distribution, since the extreme values, high or low, will have been arbitrarily eliminated in restricting the variability of the rock.

TRACE, OR MINOR, CONSTITUENTS OF AN IGNEOUS ROCK

The second and main point is connected with the fact that certain minor elements will be expected to be closely associated with some of the main constituent radicles, due to chemical combination or to similarities in ionic properties.

Three main possibilities can be envisaged:

(a) The linking between the minor constituent and its host major constituent is relatively regular, and the major constituent has a negatively-skewed distribution for its concentration values. The data for the minor constituent under these conditions would be expected to exhibit either a negatively skewed distribution, or at least an absence of a positive skewness. Since by definition the range of variation of the main constituents of a rock-type is limited, the data would also have a low dispersion.

(b) The linking between the minor and major constituents is again regular, but

the latter is one of the lesser of the main constituents and the distribution of its concentration values would therefore be of the "lognormal," or positively skewed type. Also, since it is one of the less important of the main constituents, its range of concentration would not be so limited by the conditions of definition of the rock-type. Under these conditions the minor constituent should have a positively skewed, or approximately lognormal, distribution, and an increased dispersion.

(c) The linking between the minor and major constituents may become so irregular that the distribution of the minor constituent would not be determined by that of its host constituent but by the scatter in the relationship between the two. In this event the data for the minor constituent should exhibit a positively skewed, or approximately lognormal, distribution with a relatively large dispersion. When this condition is taken to the limit, the minor constituent can be regarded as independent of other constituents.

It is of interest to study AHRENS's data (1954) in the light of these concepts. He has already drawn attention to the fact that elements showing small dispersion appear to be normally, rather than lognormally, distributed, but claims that this fact is insignificant because with such small dispersions his data are not sufficient to reveal the true nature of the distribution. The size of the dispersion and the degree of positive skewness have been related by plotting the ratio, (arithmetic mean)/(geometric mean), against the log standard deviation λ , or its square λ^2 . The fact that the second plot provides a straight-line relationship, of the type followed by a true lognormal distribution, has been taken as support for the contention of lognormality for the distributions of all elements. It is likely, however, that this evidence is not nearly so powerful as would appear at first sight. In the present context, the relationship says little more than that it becomes more and more difficult to distinguish between a normal and a lognormal distribution as the dispersion decreases. It is also clear that all the samples which it is now contended will provide exceptions to AHRENS's law fall on, or very near, the origin of the line relation a.m./g.m. to λ^2 . They would occupy this position whether their distributions were normal or lognormal, and the relationship cannot therefore give any indication that their distributions are in actual fact lognormal.

It is believed by the present author that one of the most important characteristics of AHRENS's data is the wide range of dispersions exhibited by the various elements. Thus, λ , the standard deviation of the log-concentrations, varies from 0.07 for gallium in both granite and diabase to 0.73 for chromium in diabase. On the basis of some of the concepts already discussed, this wide variation would seem to be largely due to a variation in the randomness of occurrence of the element in the igneous rock. As the element becomes more tied to one of the main constituents of the rock, so the scatter of its values conforms more to the limited scatter of the data for the main constituent. This would be accompanied by an increased tendency for the distribution of values for the trace element to follow that for the main constituent, and, as has already been pointed out, this distribution can often be negatively skewed.

It is apparent that such a concept implies a connection between the size of the dispersion and the disappearance of positive skewness which is different from AHRENS's interpretation. His view appears to be that the data with low dispersion

are in fact lognormally distributed, but that it would require many more data to show that this is so; the view of the present author is that the low dispersion implies the presence of geochemical factors which would tend to make the distribution depart from the lognormal in the direction of normality and negative skewness.

It may be shown that the arrangement of the elements in order of increasing dispersion does conform largely with the known associations of the elements with the constituent minerals of the two rocks. For this purpose it is convenient to list, as did AHRENS (1954), the elements in order of increasing dispersion of their concentration-data (Table 1). In column 3 of this table are listed the mineral, or minerals, with which each element has been reported to be associated in igneous rocks, and in column 4, the level of abundance of these minerals in granite or diabase. These levels have been taken from the modal analysis of similar materials (diabase, W-1, and granite, G-1) published by CHAYES and others (1951).

Table 1. *Host minerals of some of the trace elements of igneous rocks*

<i>Element and rock-type</i>	<i>Standard deviation of log-conc. (λ)</i>	<i>Minerals with which element may be associated in igneous rocks</i>	<i>Level of abundance of mineral in rock (per cent)</i>
Ga (d)	0.07	Minerals containing aluminium	70
Ga (gr)	0.07	Minerals containing aluminium	50
Sc (d)	0.12	Pyroxenes	45
K (gr)	0.13	Potash feldspar, micas	40
Rb (gr)	0.14	Potash feldspar, micas	40
Co (d)	0.17	Pyroxenes	45
Zr (gr)	0.18	{ Alkali minerals <i>Zircon*</i>	{ 45-75 <i>low</i>
V (d)	0.22	{ Pyroxenes <i>Magnetite*</i>	{ 45-75 <i>low</i>
La (gr)	0.28	{ Calcium minerals Potash feldspars	{ 30 35
K (d)	0.28	Potash feldspar, micas	5
Zr (d)	0.30	{ Alkali minerals <i>Zircon*</i>	{ 5-50 <i>low</i>
Cs (gr)	0.30	Potash feldspar	35
Pb (gr)	0.32	{ Potash feldspar Galena	{ 35 <i>low</i>
F (gr)	0.37	Fluorite, micas, etc.	<i>low</i>
Rb (d)	0.38	Potash feldspar, micas	5
Mo (gr)	0.42	Molybdenite	<i>low</i>
Sc (gr)	0.48	Pyroxenes	<i>low</i>
V (gr)	0.50	{ Pyroxenes <i>Magnetite*</i>	{ <i>low</i> <i>low</i>
Cr (gr)	0.54	{ Spinel <i>Pyroxenes*</i>	{ <i>low</i> <i>low</i>
Cr (d)	0.73	{ Spinel <i>Pyroxenes*</i>	{ <i>low</i> 45

* In some cases where there are two possible host minerals for an element, the less probable choice appears in italics.

There are several points of interest in the figures in this table.

(i) The six elements with the smallest dispersions, Ga(gr), Ga(d), Sc(d), K(gr), Rb(gr), and Co(d), can be positively assigned to minerals which are main constituents of the relevant rock-type. On the basis of (a) above, they might therefore be expected to show departure from a lognormal distribution. AHRENS's diagrams for four of these elements Sc(d), K(gr), Rb(gr), and Co(d) (reproduced in Figs. 3, 4, 5, and 6 of his paper) all show a slight negative skewness when passing from the linear to the logarithmic plot. Within the limitations of these data, therefore, the balance of evidence is in favour of the distributions departing from the lognormal in the direction of negative skewness.

(ii) It is illuminating to consider next the increase in the dispersion of the data for three of these elements, K, Rb, and Sc, when passing to the second rock-type. In these rocks, i.e., diabase for potassium and rubidium, and granite for scandium, the minerals with which the elements are associated are some of the lesser of the main constituents. On the basis of (b) above, therefore, the data for the minor element will follow those for the host mineral in exhibiting an increased dispersion, and a positively skewed distribution.

(iii) The remaining three elements determined by AHRENS in both rock-types, namely Zr, V, and Cr, cannot be so definitely assigned to their host minerals. However, their relative positions in Table 1 enable a choice to be made between the various minerals with which each could be associated.

Thus WICKMAN (1943) suggests reasons for the non-incorporation of zirconium in any of the common rock-forming minerals, although, on the other hand, GOLDSCHMIDT (1954) has stated that it tends to concentrate in rocks containing alkali minerals. Certain proportions of zirconium are detectable in granite as the minor mineral, zircon, but the moderate dispersion of the data for both granite and diabase, and the direction of the slight difference between these dispersions suggests a preponderating association of the element with a main constituent such as the feldspars, rather than an entirely independent occurrence.

In a similar way the data for vanadium suggest that this element is present in a mineral which is a major constituent of diabase and a less abundant constituent of granite, and the pyroxene phase would seem to satisfy this requirement.

In contrast, the marked dispersions of the data for chromium in both rocks suggest, either that the element is linked to a spinel phase rather than the pyroxene phase, or that it is unassociated in both rocks.

These aspects of AHRENS's data, while giving only limited support to the concepts outlined under (a), (b), and (c) above, do illustrate that the dispersions of concentration-data for trace constituents might have some value in elucidating the mode of association of the element with the rock.

(iv) The data for caesium in granite have a moderate dispersion, although this element is reported to be associated with a main constituent of granite, namely potash feldspar. It is suggested that the conditions visualized under (c) above would apply to caesium: the large scatter in the occurrence of the element in the feldspar outweighs the small scatter in the occurrence of the feldspar in the granite.

Lead, also, is reported to be associated with the potash feldspar of granite, and the data for this element might very well fall into the same category as those for

caesium. On the other hand, certain proportions of lead are likely to be present in granite as galena of primary origin, and the somewhat high dispersion exhibited by lead might be the effect of this contribution.

Apart, therefore, from caesium, and possibly zirconium, the dispersions of all the elements studied by AHRENS conform largely with the known relationships of the elements to other constituents of the rocks. It would be expected that the same factors which cause a decrease in the dispersion of the data for a trace element would also tend to make the distribution of data more negatively skewed. In spite of the small dispersion, coupled with the limited number of data, it is possible to detect this trend to negative skewness in some of AHRENS's plots; for the remaining data of low dispersion the plots appear to be symmetrical and they are, therefore, as likely to represent normal distributions as lognormal.

GENERAL DISCUSSION

It will be appreciated from the points already discussed that the distributions exhibited by certain trace elements will be the resultant of a negative skewness conferred by the variation in the content of the host mineral, and a positive skewness due to the randomness of the association of the trace element with the host mineral. The broadness of the classification of the rock on which observations are made would therefore have an important influence on the types of distribution which are observed. Thus, if the specification for an igneous rock is such that the main constituents cannot vary, then they cannot confer any negative skewness on the distribution of data for the trace constituent with which they are associated; the trace constituent would then be expected to exhibit a distribution of small dispersion and of positive skewness, the latter produced entirely by the scatter in the relationship between trace element and main constituent. At the one extreme the impurity elements in a mineral would be expected invariably to obey a "log-normal" law of distribution, while at the other extreme, the impurity elements in broadly classified rocks should frequently provide exceptions to such a law.

The point has already been made that, for trace elements, a "lognormal" law of distribution implies random processes in the incorporation of the element in the rock, and that as the incorporation becomes governed more and more by geochemical affinities between the trace element and the main constituent, so there will be a tendency to depart from lognormality. From this point of view the exceptions to the law proposed by AHRENS are geochemically the more interesting, and it would seem to be particularly undesirable to ignore the exceptions by accepting the law as being of general applicability to trace elements.

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Data of rock analyses—I.

African periodical and serial literature*

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PREFACE

IN 1903 the United States Geological Survey published HENRY S. WASHINGTON'S first compilation of chemical analyses of igneous rocks as Professional Paper 14, and in 1917 his final compilation as Professional Paper 99. His earlier contribution included 2881 analyses appearing in scientific publications between 1884 and 1900, and the later compilation included all those appearing between 1884 and 1913, a total of 8602. In 1952, the continuation of this work, compilation of the analyses published between 1914 and 1953, was started in the U.S. Geological Survey. The early months were devoted to consideration of the methods and procedures to be used, some of which were described in the progress report that was presented when the Commission on Geochemistry of the International Union of Chemistry met in Zurich in August 1953. This report has since been made available as an open-file report of the U.S. Geological Survey. When the project was started, the scope of the work was broadened to include the analyses of metamorphic rocks, and it was decided that publication should await the completion of the entire compilation rather than appearing in sections. Because it is apparent that publication of the analyses will be at a distant date in the future, it is our intention to publish, at appropriate intervals, such bibliographic and other pertinent data, acquired during the compilation, as seem to be valuable.

To solve the problem of how to set to work on the world literature, we decided to divide it into two general categories: (1) books or separate publications, and (2) periodical and serial publications. Assuming that the latter might be expected to contain the greater number of analyses, and having WASHINGTON'S record to use as a starting point, a world list of more than 1500 periodicals and serials was compiled, arranged by country of publication. The compilation was then begun by examination of these periodicals and serials, and first attention was directed to those published in Africa. The material presented in Part I is a list of the African periodical and serial literature arranged by country. Part II, to follow, is a bibliography, and indexes by country and by rock name, of the rock analyses from the literature in Part I.

PART I

Ex Africa semper aliquid novi—PLINY: *Historia Naturalis*.

PART I is a list of 145 African periodicals and serials that were examined. They are arranged alphabetically by country, and represent twenty-six of the forty-two political units in Africa. The other sixteen (see accompanying table for names)

* Publication authorized by the Director, U.S. Geological Survey.

Table 1. *Distribution by country of publication of the African periodical and serial literature and of the references*

Country	Publications		References (Part 2)
	Total	Current	
Algeria	12	12	10
Anglo-Egyptian Sudan	2	2	None
Angola	None	—	—
Basutoland	1	None	1
Bechuanaland	None	—	—
Belgian Congo	12	12	20
Cameroun	3	3	None
Egypt	7	7	4
Eritrea	None	—	—
Ethiopia	None	—	—
French Equatorial Africa	2	2	1
French Somaliland	None	—	—
French Togo	None	—	—
French West Africa	8	6	15
Gambia	None	—	—
Gold Coast	3	—	14
Italian Somaliland	None	—	—
Kenya	5	5	4
Liberia	None	—	—
Libya	None	—	—
Madagascar	8	7	3
Morocco (French)	7	6	7
Mozambique	1	1	None
Nigeria	3	3	3
Northern Rhodesia	3	3	None
Nyasaland	4	3	3
Portuguese Guinea	None	—	—
Sierra Leone	1	1	2
Somaliland (British)	5	3	None
Southern Rhodesia	8	7	25
South West Africa	2	2	1
Spanish Guinea	None	—	—
Spanish Morocco	None	—	—
Spanish Sahara	None	—	—
Swaziland	2	2	None
Tanganyika	6	6	7
Tangier	None	—	—
Togoland (British)	None	—	—
Tunisia	8	6	None
Uganda	8	6	7
Union of South Africa	23	18	120
Zanzibar	1	None	None
	145	126	247

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NIGERIA

Nigeria Geological Survey, Annual Report (1930-).

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NORTHERN RHODESIA

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SOUTHERN RHODESIA

National Museums of Southern Rhodesia, Occasional Papers (1932-).

—, Report (1938-). Formerly Rhodesia Museum, Annual Report.

Rhodesia Museum, Annual Report (1902-1935). See National Museums of Southern Rhodesia, Report.

Rhodesia Scientific Association, Proceedings (1899-). From 1934 on, Proceedings and Transactions.

Rhodesian Mining Journal (1927-).

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SOUTH WEST AFRICA

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TANGANYIKA

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UNION OF SOUTH AFRICA

Albany Museum Records (1903-1935).

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UNION OF SOUTH AFRICA (*continued*)

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—, Memoir (1912-).

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ZANZIBAR

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have no publications of interest to our work. Of the publications examined, only those from eighteen countries contained material germane to our compilation, as shown in the last column of the table. Ten of the twelve publications listed for the Belgian Congo are actually published in Belgium, but deal exclusively with the Belgian Congo and have been classed as African publications. With this exception, journals published outside of Africa have not been included, and references containing analyses of African rocks that appear in those journals will not be found in the bibliography in Part II.

The number of publications represents an enormous increase over the number that were available to WASHINGTON, and is accounted for in part by the establishment of many new geological organizations after the First World War, and in part by the normal publication increase during the past forty years. Although our compilation will include only material published to the end of 1953, several publications initiated in 1954 have been included in the list to make it more complete.

The name of each publication is given in unabbreviated form as it appears on the publication. For each one, the initial year of publication is given in parentheses following the name. If the periodical or serial has not ceased publication, to the best of our knowledge, the year is followed by a dash, as (1926-). If publication has ceased, the closing date is given, as (1934-1938). For those publications that have changed names in the course of years, the closing date is given under

the original name, and is then followed by a reference to the new name under which the publication has been continued. For example, we find

Egyptian University, Faculty of Science, Bulletin (1934–1938). See Fouad I University, Faculty of Science, Bulletin.

Under the new name, reference is made to the former name, as, for example,

Fouad I University, Faculty of Science, Bulletin (1939–). Formerly Egyptian University, Faculty of Science, Bulletin.

The table affords a quick appraisal of the number of publications. The countries are listed, and for each one there is given the total number of publications examined, the number currently in publication, and the number of articles from which material was compiled.

Comparison of radiogenic helium and lead in zircon*

PATRICK M. HURLEY, ESPER S. LARSEN, JR., and DAVID GOTTFRIED
Massachusetts Institute of Technology, Cambridge, Mass., and
U.S. Geological Survey, Washington 25, D.C.

(Received 4 March 1955)

ABSTRACT

A direct comparison of helium and radiogenic lead in nonmetamict zircon crystals has indicated a 25 per cent discrepancy between these radiogenic constituents. It appears that the amount of helium is only three-quarters of the amount that should be present according to the content of radiogenic lead. Approximately the same proportion was found in zircon having a wide range in age, activity, and total alpha irradiation, and in large pegmatite zircon crystals, as well as in microscopic crystals from igneous rocks.

A STUDY of helium age-ratios in zircon and sphene by HURLEY (1952) seemed to indicate a uniform increase of helium loss from these minerals, as the minerals had undergone increasing amounts of total alpha irradiation. Subsequent investigations revealed that in most samples of higher radioactivity the material is not homogeneous, some parts of the material being more radioactive and more damaged, or altered, than others. In the samples tested previously it was therefore not possible to obtain a precise relationship between alpha-radiation damage and helium loss. In particular it was not clear whether helium ratios would agree exactly with lead ratios in material that had undergone negligibly small amounts of radiation damage, and, if so, at what level of damage the helium would start to escape. It was believed that helium loss might prove to be a good indicator of the changes that occur in the process of metamictization.

A suite of gem zircon crystals from Ceylon seemed to be ideal for testing this question of helium retention. The radiogenic lead had been determined on these samples, which covered a wide range of radioactivity, and therefore radiation damage. All the samples showed the same lead age, approximately 600 million years, within limits of accuracy of the measurements. The samples were also reported to show a systematic variation in index of refraction, specific gravity (GOTTFRIED, 1953), and unit-cell dimensions, in relation to an increasing amount of radiation damage (HOLLAND and GOTTFRIED, 1955).

The results of the helium measurements on the Ceylon zircons are shown in Table 1. The first seven samples, covering a range in irradiation from 94 to 593×10^{13} α /mg, all show the same helium ratio within the limits of experimental error. From a knowledge of the radiogenic lead in each of these samples, it is found that the helium is only 77 per cent of the amount that should be present, and that this proportion does not vary despite the range of damage in the samples. In the eighth sample (No. 3038), the irradiation was up to 1070 α /mg, and the helium ratio showed the expected drop that had been observed in previous work.

A second suite of zircon samples of very different characteristics was tested in the same way. This suite is part of a group studied to determine the age of the southern California, Sierra Nevada, and Idaho batholiths by the lead-ratio method

* Publication authorized by the Director, U.S. Geological Survey.

(LARSEN *et al.*, 1954). The samples were considered to be of interest for this helium investigation because they all showed agreement in lead age (average 105 million years) and are nonmetamict, microscopic, accessory zircon, as opposed

Table 1. Helium ratios of Ceylon zircon of different activities

Sample No.	USGS No.	Alpha activity $\alpha/\text{mg/hr}$	Total irradiation $10^{13}\alpha/\text{mg}$	Helium 10^{-5} cc/g	Helium age-ratio (million years)
3031	4-33	182	94	2560	435
3001	1*	344	177	5400	485
3002	1*	401	207	6490	495
3036	3-11	525	270	7850	460
3035	2-37	678	349	10400	475
3037	2-18	890	458	13130	455
3027	2-17	1150	593	17000	455
3038	1-2	1870	1070	7870	130

Average helium age-ratio of first seven samples: 466 million years.

Average lead age-ratio of first seven samples: 600 million years.

Helium ratio/lead ratio 0.77

to the large gem crystals from Ceylon. The samples were not all homogeneous, and a few of them had to be treated with hot 1 : 1 aqua regia to remove highly radioactive grains that may have been thorite. However, after acid treatment the crystals remaining were low enough in activity, and young enough, for the radiation damage to be within the range of interest. The results of the helium measurements on these samples are given in Table 2.

Crystals of accessory zircon in igneous rocks are small enough, so that a significant fraction of the alpha particles emerge from the crystals before coming to rest. This fraction is measured by a count of alpha particles per unit time emitted by a single layer of whole crystals of known weight. Thus if I is the total activity of a sample of accessory zircon, and E is the whole-space whole-crystal emission, then I minus E gives the rate at which the number of helium atoms is increased within the boundaries of the zircon crystals.

From the results in Table 2 it again appears that the radiogenic helium is a constant proportion of the amount that should be present according to the radiogenic lead. In this case the proportion averages 70 per cent, despite a range in irradiation from 11 to $66 \times 10^{13} \alpha/\text{mg}$, which again indicates that an extrapolation to zero radiation damage would still give the same fraction.

Table 3 gives the helium ratios on a group of pegmatite zircon samples from Ontario. These samples are very low in activity (HURLEY, 1952), and therefore they probably do not contain highly radioactive zones or inclusions. They have been remeasured after acid treatment to remove any possible traces of highly active contaminant. They have been included in this investigation, together with

* Samples supplied by H. HOLLAND, Princeton University.

Table 2. Helium ratios of accessory zircon from the Southern California, Sierra Nevada, and Idaho batholiths

Sample No.	Alpha activity (α /mg/hr) I	Whole-crystal emission (α /mg/hr) E	Rate of helium increase (α /mg/hr) I - E	Total irradiation* 10^{13} α /mg	Helium 10^{-5} cc/g	Helium age-ratio (million years)
<i>Southern California batholith</i>						
3026	160	55	105	14.7	233	68
1986A	182	49	133	16.7	272	63
3033	184	48	135	16.9	342	78
1989A	237	73	164	21.8	382	72
3025	452	150	303	41.6	803	82
3030	545	183	362	50.0	805	68
1890	725	210	515	66.5	1265	76
<i>Sierra Nevada batholith</i>						
1988A	260	46	214	23.9	566	81
1990A	523	172	351	48.0	805	71
<i>Idaho batholith</i>						
1908	122	20	102	11.2	244	74
1893A	134	20	114	12.3	256	72

Average helium age-ratio : 73.

Average lead age-ratio: 105.

Helium ratio/lead ratio: 0.70.

Sample No.	USGS No.	Sample notes
3026	G-11	Green Valley tonalite, Southern California batholith.
1986A	G-15	Granite of Cottonwood Springs, Southern California batholith. Treated with aqua regia.
3033	S-1	Lakeview Mountain tonalite, Southern California batholith.
1989A	G-13 (Acid)	La Posta quartz diorite of MILLER (1935), Southern California batholith. Treated with aqua regia.
3025	S-2	Woodson Mountain granodiorite, Southern California batholith.
3030	G-48T	Stonewall quartz diorite, Southern California batholith. Treated with aqua regia.
1890	Z-14B	Rubidoux granite of LARSEN (1948), Southern California batholith.
1988A	PB-7	Granodiorite near Bishop, Calif., Sierra Nevada. Treated with aqua regia.
1990A	PB-1	Albite granite near Bishop, Calif., Sierra Nevada. Treated with aqua regia.
1908	Z-39A	Zircon concentrate from stream placer sands from the Idaho batholith. Treated with hot 1 : 1 aqua regia.
1893A	Z-39	Another sample from same locality as above. Treated with aqua regia.

* Alpha activity, times age.

the fresh part of a sample of zoned zircon from Oklahoma (LARSEN, WARING, and BERMAN, 1953), because of a good knowledge of their age by lead-ratio determination. Again it appears that the average helium ratio is approximately three-quarters of the value that would be expected, according to the age and activity of the sample.

Table 3. Helium ratios of low-activity zircon from Ontario pegmatites.
Similar samples from the same district have been dated by lead ratios.

Sample No.	Locality	Alpha activity (α /mg/hr)	Helium 10^{-5} cc/g	Helium age-ratio (million years)
1659	Renfrew County, Ontario	31	780	770
1777	Renfrew County, Ontario	32	797	770
1660	Brudenell Township, Ontario	32	742	715
1681	S. Burgess, Leeds County, Ontario	32	715	700
1670	Lanark County, Ontario	68	1618	730
1901	Fresh part of zoned zircon from Oklahoma (treated with aqua regia) Average lead age of same crystal: 635 million years Helium ratio/lead ratio 0.71	150	2190	450

Average helium age-ratio of first five samples: 737 million years.

Average lead age of pegmatites from same region: 1000 million years.

Helium ratio/lead 0.73.

The accuracy of the measurements listed in the tables must be stated in qualitative terms. The measurements of activity have a basic precision set by counting statistics: generally counts are made so that this error is not greater than 2 per cent standard deviation. In addition, a variation in source area and in inhomogeneity in the sample may raise the total error in precision to about 5 per cent per analysis. Exceptionally inhomogeneous material may show greater variations. The determination of the activity in thick sources of the samples requires the use of a source absorption factor. In zircon, a factor of 0.493 was calculated for the conversion from α /cm²/hr to α /mg/hr for an assumed Th/U ratio of 1. This factor is known to be approximately correct from independent measurements of uranium and thorium. However, in this investigation an error in this factor, or in the activity measurements themselves, is not significant, as the same values are used for both the helium and lead ratios.

The helium measurements normally have a precision of about 6 per cent as determined by replicate measurements of materials containing amounts of helium in this range. The absolute accuracy of the helium analysis is believed to be within 5 per cent. The McLeod gauge was calibrated well within this limit by

weight of mercury; and the calibration of the entire analysis procedure, using measured samples of helium introduced in blank fusions, has established the calibration constant for the system over a period of years. An independent measurement using a new pipette for the introduction of a known amount of helium gave a result agreeing within 3 per cent of the standard calibration value. As the helium analyses listed show the same ratio despite a variation in helium content of the sample from 240 to $17,000 \times 10^{-5}$ cc/g, there seems to be little possibility that the analyses are low because of incomplete release of helium in the fusion.

A process of helium loss that would leave the same proportion of helium remaining in the crystalline material despite differences in helium content and age, is not yet visualized by the authors. The question will have to remain open until other evidences can be brought to bear on it.

ACKNOWLEDGEMENTS

The authors wish to thank Professor HEINRICH HOLLAND of Princeton University for the samples supplied by him. This research was conducted by the U.S. Geological Survey on behalf of the Division of Research of the U.S. Atomic Energy Commission. The instruments used in the investigation were made available by the Office of Naval Research, U.S. Department of Defence.

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News and Notes

Consultants Bureau, New York, are publishing, beginning with 1956, translations of the entire Geochemical Section of the Doklady (Proc. Nat. Acad. Sci., U.S.S.R.). Table of contents (translations), free on request.

ANNOUNCEMENTS

Geochemical Society Organized

At the recent meetings of the Geological Society of America (New Orleans, 7 November) organization of the Geochemical Society was completed. A constitution was adopted which specifies that "The object of the society shall be to encourage the application of chemistry to the solution of geological and cosmological problems" and that "any person who is qualified to advance the objects of the society shall be eligible for membership." This includes physicists, biologists, mathematicians, oceanographers, meteorologists, etc., as well as chemists and geologists.

The following officers were elected: President, EARL INGERSON, U.S.G.S., Washington; Vice-President, JULIAN R. GOLDSMITH, University of Chicago; Secretary, JOHN C. MAXWELL, Princeton University; Treasurer, GEORGE T. FAUST; Councillors-at-Large, J. W. GREIG, W. F. LIBBY, W. T. PECORA, W. W. RUBEY, G. R. TILTON, and H. S. YODER.

Persons wishing to become charter members should send their names, addresses, fields of interest, and a year's dues (\$2) to the Treasurer, Dr. GEORGE T. FAUST, U.S. Geological Survey, Washington 25, D.C.

Predoctoral Fellowships in Petrology and Geochemistry

Two predoctoral fellowships are offered jointly by the Geophysical Laboratories of the Carnegie Institution, Washington, D.C., and the Johns Hopkins University, Baltimore, Maryland. The fellowships cover a two- to three-year period. The stipend for the first academic year is \$2400. During this year the fellowship holder is chiefly engaged in course work at the university. Starting with the second year he will normally spend most of his time at the geophysical laboratories working on a problem for his dissertation. Duration of this period is variable and may amount to approximately two years. The stipend for this period starts at \$200 per month plus provision for university tuition and is increased to \$225 per month during the concluding period of tenure.

Application for the fellowship, supported by transcripts and recommendations, must be sent to Professor ERNST CLOOS, Geology Department, The Johns Hopkins University, Baltimore 18, Maryland, prior to 1 March.

Erratum

In "The Occurrence of Magnesian Calcites in Nature" by JULIAN R. GOLDSMITH, DONALD L. GRAF, and OIVA I. JOENSUU, pp. 212-230, Vol. 7, 1955, credit should be given to the Grönlands Geologiske Undersökelse, Copenhagen, Denmark, for the West Greenland samples.

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to honour

Henry Bryant Bigelow

EDITED BY DR. MARY SEARS

This volume, published as a supplement to the journal *Deep-Sea Research*, contains both original research papers and review articles prepared by DR. BIGELOW's colleagues and students to honour him on the occasion of the twenty-fifth anniversary of the Woods Hole Oceanographic Institution, with which he has been intimately associated since its inception. The wide scope of the subjects covered in the various articles ensures its appeal not only to oceanographers and other research workers in allied fields, but also to fisheries biologists and those con-

cerned with problems of the continental shelf.

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The book has 498 pages of text and includes 48 articles. There are 118 diagrams and 30 photographs, plus eight illustrations in colour. It is of the same size as *Deep-Sea Research* and is supplied fully bound in a green cloth.

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